1. PHYSICAL AND TECHNICAL BASES OF MÖSSBAUER SPECTROSCOPY


1.1. INTRODUCTION

The phenomenon of recoil-free resonant emission and absorption of nuclear gamma-rays was discovered in 1958 by Mössbauer [1]. The discovery achieved a resounding success because of its unique relative energy resolution. In the beginning Mössbauer effect was expected to contribute first of all to nuclear physics but later on (especially after the easily detectable resonance of the nuclide $^{57}$Fe has been discovered [2, 3]) it turned out that the possible applications of the method are even more important. The first (and perhaps up to now most spectacular) application of the method was the demonstration of the gravitational red shift of gamma-rays [4]. The wide variety of applications in solid state physics and chemistry was open by the demonstration of various hyperfine (magnetic dipole [2], electric quadrupole [5] and isomer [5]) interactions.

Nowadays there are a lot of general works (e.g. [6–14]) on Mössbauer spectroscopy where the foundations and applications are described in detail. Therefore in Chapter 1 we only attempt to give a brief introduction to the theory and methodology of Mössbauer spectroscopy for beginners in the field to an extent which is necessary for the understanding of the further chapters.

1.2. RECOIL-FREE NUCLEAR RESONANCE EMISSION AND ABSORPTION

Consider a fixed nucleus which is in an excited state of energy $E_0$. If this nucleus is decaying electromagnetically to the ground state a photon of energy $E$ will be emitted with a probability density:

$$W_e(E) = \frac{\Gamma}{2\pi} \frac{1}{(E - E_0)^2 + \frac{\Gamma^2}{4}} \frac{1}{1 + \alpha} \quad (1.1)$$

where $\alpha$ is the coefficient of the internal conversion (the average number of internal conversions is $\alpha$ while one photon is emitted) and $\Gamma$ is the natural linewidth. $\Gamma$ is connected to the lifetime $\tau$ of the excited state by Heisenberg's uncertainty relation:

$$\Gamma \tau = \hbar \quad (1.2)$$

where $\hbar$ is the Planck constant divided by $2\pi$.  

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Another similar nucleus which is in the ground state will absorb this photon of energy $E$ with a cross-section:

$$\sigma(E) = \frac{\omega}{4} \frac{1}{(E - E_0)^2 + \frac{1}{4} \Gamma^2} \frac{1}{1 + \alpha}$$  \hspace{1cm} (1.3)$$

where $\sigma_0 = \sigma'_0/(1 + \alpha)$ is the maximum cross-section of the resonance absorption. $\sigma'_0$ is given by

$$\sigma'_0 = 2\pi\hbar^2 c^2 \frac{2I_\pi + 1}{2I_\pi + 1} \frac{1}{E_0^2}.$$  \hspace{1cm} (1.4)$$

Here $I_\pi$ is the nuclear spin of the excited state, $I_\pi$ is that of the ground state and $c$ is the velocity of light.

The effective cross-section for the resonance absorption is

$$\sigma_{\text{eff}} = \int_0^\infty W_\pi(E)\sigma(E)\,dE.$$  \hspace{1cm} (1.5)$$

If the nucleus is free it will receive the recoil energy

$$E_R = \frac{E_0^2}{2M c^2}$$  \hspace{1cm} (1.6)$$

by the emitted photon where $M$ is the mass of the nucleus. The energy of the photon will be decreased by $E_R$. Thus, the emission line $W'_\pi(E)$ appears at the energy $E_0 - E_R$ rather than at $E_0$:

$$W'_\pi(E) = W_\pi(E + E_R).$$  \hspace{1cm} (1.7)$$

The line of the absorption cross-section $\sigma'(E)$ will be shifted by the same amount to higher energies:

$$\sigma'(E) = \sigma(E - E_R).$$  \hspace{1cm} (1.8)$$

The effective cross-section is now:

$$\sigma'_{\text{eff}} = \int_0^\infty W'_{\pi}(E) \sigma'(E)\,dE = \int_0^\infty W_\pi(E + E_R) \sigma(E - E_R)\,dE,$$  \hspace{1cm} (1.9)$$

which will only be significant if

$$2E_R \leq \Gamma.$$  \hspace{1cm} (1.10)$$

(See Fig. 1.1). For many electromagnetic nuclear transitions $E_R \approx 10^{-2} \ldots 10^{-3}$ eV while $\Gamma \approx 10^{-7} \ldots 10^{-9}$ eV. Condition (1.10) is not fulfilled at all which is why the cross-section of resonant absorption on free nuclei is extremely small.

The situation will completely be different if the emitting and absorbing nucleus is embedded in solids. In this case the recoil energy will be transferred to the system of lattice vibrations since a few meV are insufficient to knock out an atom from its original site. It was shown by Mössbauer [1] that under such circumstances a processes during which the state of the system of lattice vibrations is unchanged may have a considerable probability. Thus, the emission and absorption of the photon will be recoil-free. This phenomenon is the Mössbauer effect.
Fig. 1.1. The emission line $\textit{W}'(E)$ and the absorption line $\sigma'(E)$ of $\gamma$-transitions on free nuclei.

The probability $f$ of the recoil-free process is essentially described by the same Debye–Waller factor which gives the fraction of elastic processes in X-ray and neutron diffraction:

$$f = e^{-k^2\langle x^2 \rangle}.$$ (1.11)

Here $k$ is the wave-number of the photon while $\langle x^2 \rangle$ is the mean square displacement of the resonant nucleus in the photon propagation direction.

The theory of the recoil-free fraction will be discussed in somewhat more detail later on in Section 1.6 along with diffusion line broadening effects. At this point it should only be mentioned that in the frame of a concrete model of lattice vibrations the probability of the Mössbauer effect at various temperatures can be calculated.

For a Debye model:

$$f = \exp \left\{ \frac{-6E_R}{k_B \theta_D} \left[ \frac{1}{4} + \left( \frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{y \, dy}{e^y - 1} \right] \right\}. $$ (1.12)

Here $k_B$ is the Boltzmann constant, $T$ is the temperature and $\theta_D$ is the Debye temperature of the crystal. In practice the asymptotic forms of Eq. (1.12) can be very useful:

$$f = \exp \left[ \frac{-E_R}{k_B \theta_D} \left( \frac{3}{2} + \frac{\pi^2 T^2}{\theta_D^2} \right) \right], \quad \text{if} \quad T \ll \theta_D $$ (1.13)

$$f = \exp \left( \frac{-6E_R T}{k_B \theta_D^2} \right), \quad \text{if} \quad T \gg \frac{\theta_D}{2}. $$ (1.14)

It can be seen from Eq. (1.13) that the probability of the Mössbauer effect does not reach unity even at $T=0$:

$$f(T=0) = \exp \left( \frac{-3E_R}{2k_B \theta_D} \right). $$ (1.15)

Comparing Eq. (1.15) with Eq. (1.11) one can see that the reason for this fact is that $\langle x^2 \rangle > 0$ even at $T=0$ because of the quantum-mechanical zero-point motion of nuclei.

A detectable Mössbauer effect can be expected if the value of the product $n\sigma\sigma$ is high enough. Here $n$ is the number of resonant nuclei per unit area of the absorber. From Eqs (1.6), (1.12) and (1.14) one can see that in this case $E_0$ must not be too high. This is why the effect can hardly be detected at gamma-ray energies above 100 keV. Below
ca 5 keV the atomic absorption of the gammas increases dramatically with decreasing energy. Thus, detection problems arise. It is difficult to detect too narrow and too broad resonance lines by conventional methods. Therefore, according to Eq. (1.2), the lifetime of the excited state should be, as a rule, between $10^{-10}$ and $10^{-6}$ s. From Eqs (1.1) and (1.3) it can be concluded that the probability of internal conversion must not be too high ($\alpha \leq 10$). According to Eq. (1.12), the probability of the Mössbauer effect will be high if $T$ is low and $\theta_D$ is high. Finally, the relative abundance of the resonant nuclide should be high enough. All these conditions are best fulfilled for the 14.4 keV transition of $^{57}$Fe (Fig. 1.2). Easily detectable Mössbauer transitions have some further nuclides: $^{61}$Ni, $^{99}$Ru, $^{119}$Sn, $^{121}$Sb, $^{125}$Te, $^{129}$I, $^{151}$Eu, $^{155}$Gd, $^{161}$Dy, $^{169}$Tm, $^{197}$Au, $^{237}$Np, etc.

![Diagram](image)

Fig. 1.2. Decay scheme of $^{57}$Co

Table 1.1 summarizes the most important parameters of Mössbauer transitions. Mössbauer effect is generally measured by scanning the absorption lines. In most cases the absorption line is not a Lorentzian centred at $E_0$ since, as it will be shown in Section 1.3, hyperfine interactions can shift and split it by about $10^{-6}$ eV. The shape of the absorption line can be scanned by changing the energy of the source along a range in this order of magnitude. The most general way to achieve this change is to move the source. If the source is moving with a velocity $v$ relative to the absorber then the mean energy of photons emitted towards the absorber is

$$E(v) = E_0 \left(1 + \frac{v}{c}\right).$$

(1.16)

As it can be realized from Table 1.1, in most cases (e.g. $^{57}$Fe) the source should be moved with a velocity of several mm s$^{-1}$.

The photons emitted by the source and crossing the absorber are detected behind the absorber (Fig. 1.3) as a function of the velocity of the source. The number of counts $N(v)$ detected during a certain time is called Mössbauer spectrum. In many cases the
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<th>Spin and parity of the excited state</th>
<th>Spin and parity of the ground state</th>
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<th>Half life, ns</th>
<th>Linewidth, mm/s</th>
<th>Internal conversion coefficient, $\alpha$</th>
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<td>Isotope abundance, %</td>
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<td>Linewidth, mm/s</td>
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<td>Maximum resonance cross-section, $\sigma_{0}$, $10^{-26}$ cm$^2$</td>
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<td>3/2(^+)</td>
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<td>1/2(^-)</td>
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<td>17.1</td>
<td>7.2</td>
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<td>3/2(^+)</td>
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<td>0(^+)</td>
<td>0 (a)</td>
<td>0.37</td>
<td>13.9</td>
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<tr>
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<td>0(^+)</td>
<td>100 (a)</td>
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<td>3/2(^-)</td>
<td>0 (a)</td>
<td>45.1</td>
<td>0.072</td>
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<td>0(^-)</td>
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<td>24.9</td>
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<td>67</td>
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<td>0 (a)</td>
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<td>0 (a)</td>
<td>2.34</td>
<td>1.39</td>
<td>0.3</td>
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* Compiled from several issues of the Mössbauer Effect Data Index (J. G. Stevens and V. E. Stevens, University of Asheville, USA) and from the Decay Schemes and Parameters of Mössbauer Isotopes (D. Barb and M. Morariu, Central Institute of Physics, Bucharest, Roumania, 1978).
normalized spectrum is used:

\[ S(v) = \frac{N(\infty) - N(v)}{N(\infty)}. \]  

(1.17)

Here \( v = \infty \) means a velocity far off resonance.

Using Eq. (1.16), the energy in Mössbauer spectroscopy is generally given in velocity units. This convention will be used throughout this book.

1.3. **HYPERFINE INTERACTIONS**

1.3.1. **HYPERFINE SPLITTING OF NUCLEAR LEVELS**

Nuclei interact with surrounding electrons. This results in the hyperfine splitting of optical spectra. That is why this kind of interaction is called “hyperfine”. The energy of hyperfine interactions generally does not exceed \( 10^{-6} \) eV so that before Mössbauer's discovery it was completely impossible to observe directly the hyperfine splitting of nuclear transitions their energy being by about 10 orders of magnitude higher. However, the appearance of a component of natural linewidth in the spectrum of nuclear resonance absorption ensures the necessary resolution.

The study of hyperfine interactions is of basic importance since, as we shall see, it yields many information regarding the electronic structure of the environment of the nucleus.

As a consequence of hyperfine interactions the nucleus is subjected to very intense electric and magnetic fields. These interactions can be described by classical electrodynamics.

The nucleus has an electric charge distribution \( e \rho(r) \) (\( e \) is the charge of the proton; the origin of the coordinate system is the centre of mass of the nucleus). The electrostatic field of external charges (electrons, other ions, etc.) is described by the potential \( V'(r) \). The electrostatic energy is then

\[ H_{\text{el}} = e \int \rho(r) V'(r) d^3r. \]  

(1.18)

\( V'(r) \) can be expanded in terms of \( \mathbf{r} \) around \( r = 0 \):

\[ V'(r) = V'(0) + \sum_{i=1}^{3} V_i'(0)x_i + \frac{1}{2} \sum_{i,k=1}^{3} V_{ik}'(0)x_i x_k + \ldots \]  

(1.19)
Here $x_i$ is the $i$-th coordinate of the radius vector $r$ while $V''_i = \frac{\partial V'}{\partial x_i}$ and $V''_{ik} = \frac{\partial^2 V'}{\partial x_i \partial x_k}$.

Substituting Eq. (1.19) into Eq. (1.18) and taking into account that

$$
\sum_{i,k} V''_{ik}(0) \delta_{ik} = \sum_i V''_i(0) = \Delta V'(r)|_{r=0} = 4\pi e \rho'(0),
$$

(1.20)

we obtain the following expression for the interaction energy:

$$
H_m = e \int \rho(r) \left[ V'(0) + \frac{2}{3} \pi r^2 e \rho'(0) + \sum_i V''_i(0) x_i + \frac{1}{2} \sum_{i,k} V''_{ik}(0) \left( x_i x_k - \delta_{ik} \frac{r^2}{3} \right) \right] d^3 r.
$$

(1.21)

Here, $\rho'(0)$ is the density of the negative charges responsible for $V'(r)$ at the origin. $\Delta$ is the Laplace operator.

The quadrupole moment tensor of the nucleus is

$$
Q_{ik} = \int \rho(r) (3 x_i x_k - \delta_{ik} r^2) d^3 r
$$

(1.22)

with the use of this notation and

$$
\langle R^2 \rangle = \frac{\int \rho(r) r^2 d^3 r}{\int \rho(r) d^3 r} = \frac{1}{Z} \int \rho(r) r^2 d^3 r
$$

(1.23)

the interaction energy becomes

$$
H_m = e Z V'(0) + \frac{2}{3} \pi e^2 Z \rho'(0) \langle R^2 \rangle +
$$

$$
+ e V''_i(0) \int \rho(r) x_i d^3 r + \frac{1}{6} e \sum_{i,k} V''_{ik}(0) Q_{ik}.
$$

(1.24)

Here $Z$ is the number of protons in the nucleus.

The third term on the right side of Eq. (1.24) vanishes, the integral being the electric dipole moment of the nucleus. The parity of nuclei is a constant of motion (the nuclear wave function is either even or odd) which is why the charge density function is always even. Therefore the integrand is odd and the integral (the dipole moment) should be zero.

The non-vanishing terms in Eq. (1.24) have very direct meaning. The first term describes the Coulomb energy of a point charge, the second term is the contribution from the finite extension of the nucleus while the last term is the energy of quadrupole interaction.

For the charge density distribution of the nucleus a very simple model is often used: the nucleus is considered to be a homogeneously charged sphere of radius $R$. Such an approximation can be obviously used only for calculating $\langle R^2 \rangle$ and not of $Q_{ik}$ the latter describing just the deviation of $\rho(r)$ from the spherical symmetry. With the charge
distribution

\[ \rho(r) = \begin{cases} \frac{3Z}{4\pi R^3} & \text{if } r \leq R \\ 0 & \text{if } r > R \end{cases} \]  

(1.25)

one obtains

\[ \left\langle R^2 \right\rangle = \frac{3}{5} R^2. \]  

(1.26)

The tensor \( V_{ik} \) is the second derivative of the electrostatic potential. Thus, apart from its sign, it is the vector gradient of the electric field strength. Generally, however, another tensor is called electric field gradient (EFG) which can be obtained from \( V_{ik} \) by eliminating its trace:

\[ V_{ik} = V_{ik} - \frac{1}{3} \delta_{ik} \sum_j V_{jj}. \]  

(1.27)

Using Eq. (1.27) and the fact that according to Eq. (1.22)

\[ \sum_i Q_{ii} = 0, \]  

(1.28)

\( V_{ik} \) can be replaced in Eq. (1.24) by \( V_{ik} \). Using Eq. (1.26) and taking into account that the nucleus has a magnetic dipole moment \( \mu \) for the interaction energy, we have the form

\[ H_M = eZV(0) + \frac{2\pi}{5} e^2 \rho'(0) Z R^2 + \frac{1}{6} e \sum_{i,j} V_{ik}(0) Q_{ij} - \sum_j \mu_j H_j. \]  

(1.29)

Here \( H \) is the magnetic field strength acting on the nucleus.

\( Q_{ik} \) can be characterized by a single number:

\[ Q = \int \rho(r) r^2 (3 \cos^2 \theta - 1) d^3r, \]  

(1.30)

which is equal to \( Q_{xx} \) if \( Q_{ik} \) is diagonalized so that the \( z \) axis is parallel to the direction of the nuclear spin \( I \). The other two diagonal elements are then \( Q_{xx} = Q_{yy} = -Q/2 \) since the nucleus is axially symmetric around the \( z \) axis.

It can be shown [15] that the equivalent operator of \( Q_{ik} \) in quantum mechanics is:

\[ \hat{Q}_{ik} = \frac{3Q}{2I(2I-1)} \left[ \hat{I}_k \hat{I}_k + \hat{I}_k \hat{I}_k - \frac{2}{3} \hat{I}^2 \delta_{ik} \right]. \]  

(1.31)

In the principal axis system of \( V_{ik}(0) \) where

\[ V_{ik}(0) = V_{ii}(0) \delta_{ik}, \]  

(1.32)

the equivalent operator of the third term of Eq. (1.29) is

\[ \hat{H}_Q = \frac{e}{6} \sum_i V_{ii}(0) \hat{Q}_{ii} = \frac{eQ}{4I(2I-1)} \sum_i (2 \hat{I}_i^2 - 2 \frac{2}{3} \hat{I}^2) = \]  

\[ = \frac{eQ}{2I(2I-1)} \left[ V_{xx}(0) \hat{I}_x^2 + V_{yy}(0) \hat{I}_y^2 + V_{zz}(0) \hat{I}_z^2 \right]. \]  

(1.33)
Here the property
\[ V_{xx} + V_{yy} + V_{zz} = 0 \] (1.34)
following from Eq. (1.27) has been used. Equation (1.34) means that only two of \( V_{xx} \), \( V_{yy} \), and \( V_{zz} \) are independent. (Further on the argument 0 of \( V_k \) will be omitted.) The coordinate axes are labelled so that
\[ |V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \] (1.35)
The EFG tensor is described by two quantities namely \( V_{zz} \) and the asymmetry parameter
\[ \eta = \frac{V_{xx} - V_{yy}}{V_{zz}}. \] (1.36)
With the use of these parameters Eq. (1.33) can be re-written as
\[ \hat{H}_Q = \frac{eQV_{zz}}{4I(2I-1)} \left[ 3I_z^2 - I(I+1) + \eta(I^+ - I^-) \right] \] (1.37)
or
\[ \hat{H}_Q = \frac{eQV_{zz}}{4I(2I-1)} \left[ 3I_z^2 - I(I+1) + \frac{\eta}{2}(I^+ + I^-) \right] \] (1.38)
where
\[ I_+ = I_x + iI_y \] (1.39)
\[ I_- = I_x - iI_y. \] (1.40)
If the EFG is axially symmetric (\( \eta = 0 \)) the eigenstates of \( \hat{I}_z \) are the eigenstate of \( \hat{H}_Q \) while the eigenvalues are
\[ E_Q = \frac{eQV_{zz}}{4I(2I-1)} \left[ 3m^2 - I(I+1) \right] \] (1.41)
where \( m \) is the magnetic quantum number belonging to \( \hat{I}_z \). If \( \eta \neq 0 \) the eigenvalues cannot be given generally in a closed form. In one of the most important cases (\( I = 3/2 \)), however, a closed expression exists:
\[ E_Q = \frac{eQV_{zz}}{4} \left( m^2 - \frac{5}{4} \right) \sqrt{1 + \frac{\eta^2}{3}}. \] (1.42)
The last term of Eq. (1.29) describes the Zeeman splitting of nuclear levels:
\[ \hat{H}_M = -\mu H = -g\mu_N \hat{I} \] (1.43)
where \( g \) is the \( g \)-factor of the nuclear level, while \( \mu_N \) is the nuclear magneton. Of course, if the magnetic field is parallel to the \( z \) axis the eigenstates of \( \hat{H}_M \) are the eigenstates of \( \hat{I}_z \) with the eigenvalues
\[ E_M = -g\mu_N H m. \] (1.44)
Coming now to the perturbation of the energy of the \( \gamma \)-transition the excited and the ground state of the nucleus is split corresponding to the eigenvalues of \( \hat{H}_M^e \) and \( \hat{H}_M^g \), where \( \hat{H}_M^e \) and \( \hat{H}_M^g \) denote the Hamiltonian (1.29) in the excited and ground state of the nucleus, respectively. The first term on the right side of Eq. (1.29) being the same in both
states of the nucleus does not appear in the transition energy. The second term leads to a shift of the spectral lines:

$$\delta = \frac{2\pi}{3} e^2 \rho'(0) Z (\langle R_e^2 \rangle - \langle R_g^2 \rangle) = \frac{2\pi}{5} e^2 \rho'(0) Z (R_e^2 - R_g^2) = \frac{4\pi}{5} e^2 \rho'(0) Z R^2 \frac{\delta R}{R},$$

(1.45)

where $R_e$ and $R_g$ are the nuclear radius in the excited and ground state, respectively; $\delta R = R_e - R_g$, $R = (R_e + R_g)/2$. $\delta$ is the isomer shift.

If the EFG is axially symmetric and its axis is parallel to $H$ then the energy of the transition between the states $|I_e, m_e\rangle$ and $|I_g, m_g\rangle$ is

$$E_0 = E_0 + \frac{4\pi}{5} e^2 Z \rho'(0) R^2 \frac{\delta R}{R} + \left\{ \frac{Q_e}{4I_e(2I_e - 1)} [3m_e^2 - I_e(I_e + 1)] - \right.$$

$$- \frac{Q_g}{4I_g(2I_g - 1)} [3m_g^2 - I_g(I_g + 1)] \right\} eV_{zz} + (m_gg_g - m_eg_e) \mu_N H$$

(1.46)

where the indices $g$ and $e$ refer to the ground and excited states, respectively. The third term (on the right side) of Eq. (1.46) is the electric quadrupole shift (splitting) and the fourth term the magnetic dipole shift (splitting).

In the case of a $1/2 \rightarrow 3/2$ transition

$$E_0 = E_0 + \frac{4\pi}{5} e^2 Z \rho'(0) R^2 \frac{\delta R}{R} + \frac{eQ_e V_{zz}}{4} \left( m_e^2 - \frac{5}{4} \right)$$

$$+ (m_gg_g - m_eg_e) \mu_N H.$$

(1.47)

All the three perturbing energy terms are the products of a nuclear and a solid-state factor. The positions of the split and shifted resonance lines generally determine the value of every single term of Eq. (1.47). Once the nuclear factors $[R^2(\delta R/R)]$, $Q_g$, $(m_gg_g - m_eg_e)$ have been measured the solid-state factors $[\rho'(0), V_{zz}, H]$ can be calculated.

Sources in Mössbauer spectroscopy are mostly substances without electric quadrupole and magnetic dipole interaction. Their spectrum consists, therefore, of a single unsplit line of natural width. Isomer shifts cannot, of course, be switched off. That is why the energy of a photon emitted by the source exceeds the transition energy $E_0$ of the free nucleus by

$$\delta_s = \frac{4\pi}{5} e^2 Z |\Psi_s(0)|^2 R^2 \frac{\delta R}{R},$$

(1.48)

where $\Psi_s(0)$ is the wave-function of the electrons at the nucleus in the source.

So, if the absorber has neither electric quadrupole nor magnetic dipole interaction the spectrum will consist of a single line at

$$\delta = \frac{4\pi}{5} e^2 Z \left( |\Psi_s(0)|^2 - |\Psi_s(0)|^2 \right) R^2 \frac{\delta R}{R},$$

(1.49)

where $\Psi_s(0)$ is the wave-function of the electrons at the nucleus in the absorber.
In the case of a $1/2 \rightarrow 3/2$ dipole transition, if the electric quadrupole interaction differs from zero the spectrum will be a doublet while the magnetic dipole interaction will result in a six-line pattern according to the selection rule $\Delta m = 0, \pm 1$.

In the case of a combined magnetic dipole/electric quadrupole interaction the position of the spectral lines generally cannot be given via closed form even for a $1/2 \rightarrow 3/2$ transition. If $|eQV_{zz}| \ll |\mu H|$ then the first order perturbation theory can be applied. If the EFG is axially symmetric and the angle of $H$ to the $z$ axis is $\vartheta$ then the eigenvalues of $\hat{H}_Q + \hat{H}_M$ are:

$$E = -g \mu_N H m + (-1)^{|m|} + \frac{1}{2} \frac{eQV_{zz}}{4} \frac{3 \cos^2 \vartheta - 1}{2} \quad (1.50)$$

The value of $\vartheta$ is often unknown. In such cases

$$\varepsilon = \frac{eQV_{zz}}{4} \frac{3 \cos^2 \vartheta - 1}{2} \quad (1.51)$$

is used. The electric quadrupole interaction shifts the two outermost lines of the sextet by $\varepsilon$ while the four inner lines by $-\varepsilon$ (Fig. 1.4). In more complex cases the line positions can only be numerically calculated from the parameters of hyperfine interaction.

![Diagram](image)

Fig. 1.4. Splitting of a $1/2 \rightarrow 3/2$ dipole transition in the case of magnetic dipole and combined hyperfine interaction

For a complete description of the spectrum besides the line positions the line intensities are also necessary. We shall come back to this problem in Section 1.5.

The basic problem of Mössbauer spectroscopy is the quantitative description of the electron density, electric field gradient and magnetic field in terms of the electron structure of the crystal.
The isomer shift is proportional to the electron density at the nucleus. Classically only the s electrons have a non-vanishing density at the nucleus. Relativistically, however, the p_{1/2} electrons also contribute to the electron density at the nucleus. In most cases this relativistic correction can be neglected.

The relativistic correction of the density of the s electrons is very essential. Instead of Eq. (1.49) the isomer shift is given by

\[ \delta = S'(Z) \frac{4\pi}{5} e^2 Z \left[ |\Psi_s(0)|^2 - |\Psi_s(0)|^2 \right] R^2 \frac{\delta R}{R} \]  \hspace{1cm} (1.52)

where \( \Psi_s \) and \( \Psi_s \) denote the non-relativistic wave-functions. \( S' \) is a rapidly increasing function of \( Z \); its value for Fe is 1.29.

Although only the s electrons have a considerable density at the nucleus the other electrons also contribute to the isomer shift. For example, an increasing number of 3d electrons leads to an enhanced shielding of the 3s electrons and results in a decrease of \( |\Psi(0)|^2 \). This means an increase in the isomer shift of \(^{57}\text{Fe}\) since the 14.4 keV transition of this nucleus the nuclear radius in the excited state is less than that in the ground state. This behaviour offers a possibility for determining the valence state of the investigated ion since, for example, the isomer shift of the high-spin \(^{3+}\text{Fe}\) [electron configuration: \((3d)^{5}\)] differs from that of the high-spin \(^{2+}\text{Fe}\) [electron configuration: \((3d)^6\)] by about ten natural linewidths. Figure 1.5 shows some typical isomer shifts of \(^{57}\text{Fe}\). Conventionally the isomer shift of \(\alpha\)-Fe at room temperature is chosen to be zero.

The quantitative interpretation of the \(^{57}\text{Fe}\) isomer shifts has been attempted many times though the problem has not been completely solved yet. Walker, Wertheim and

![Diagram](image)

*Fig. 1.5. Typical isomer shifts of iron compounds*
Jaccarino (WWJ) [17] calculated $|\Psi(0)|^2$ for the (3d)$^5$ and (3d)$^6$ configurations by free ion Hartree–Fock calculations. Then, comparing the obtained values of $|\Psi(0)|^2$ with the isomer shift of some highly ionic Fe$^{3+}$ and Fe$^{2+}$ compounds, respectively, the calibration factor between $\delta$ and $|\Psi(0)|^2$ was determined. The chemical bond gets more covalent by the appearance of 4s electrons. Since 4s electrons do not shield considerably the inner s electrons their contribution can be accounted separately. The results of the WWJ model are shown in Fig. 1.6 [17].

Later on, the above interpretation has been improved [18]. It has been concluded from molecular orbital (MO) calculations that the Fe$^{3+}$ ion is never fully ionic because at least 0.3–0.4 4s electrons are back-donated by the surrounding ligands. This decreases the estimated absolute value of $\delta R/R$. From the WWJ model $\delta R/R = -18 \times 10^{-4}$ while after Danon’s correction [18] $\delta R/R = -7 \times 10^{-4}$.

Since the starting point of the mentioned models is a free ion Hartree–Fock calculation, they cannot account for the isomer shift either of the low spin Fe$^{(II)}$ and Fe$^{(III)}$ ions existing in strong crystal fields or of covalent diamagnetic complexes (e.g. ferrocene). In these cases only MO calculations can be applied. Also for metallic systems special care should be paid.

The isomer shift is, of course, pressure-dependent since $|\Psi(0)|^2$ can be changed by compression. This offers a further possibility of estimating $\delta R/R$. 
A shift of the spectral lines is caused by the second order Doppler effect coming from the thermal motion of atoms. Though this shift is not a consequence of hyperfine interaction it is mentioned here since it cannot be measured independently from the isomer shift.

If a nucleus emitting in its own system a photon of frequency \( v \) is subject to a thermal motion of velocity \( v_T \), then the observed mean frequency is

\[
v' = v \left( 1 - \frac{\langle v_T^2 \rangle}{2c^2} \right).
\]

This leads to a shift of

\[
\delta E_D = -\frac{\langle v_T^2 \rangle}{2c^2} E_0 = -\frac{U}{2c^2} E_0
\]

of the spectral lines where \( U \) is the specific internal energy of the crystal because the mean kinetic energy of a harmonic oscillator is the half of its total energy:

\[
\frac{1}{2} M \langle v_T^2 \rangle = \frac{1}{2} M U.
\]

In the Debye approximation of a lattice containing one kind of atoms [9]:

\[
\delta E_D = -\left[ \frac{9}{16} \frac{k_B \theta_D}{M c^2} + \frac{3}{2} \frac{k_B T}{M c^2} f_D \left( \frac{T}{\theta_D} \right) \right].
\]

Here

\[
f_D(y) = 3 y^3 \int_0^{1/y} \frac{x^3}{e^x - 1} \, dx
\]

is the Debye function. Since \( f_D(y) = 1 \) if \( y \gg 1 \) at high temperatures the energy of the resonance line is decreasing linearly with increasing temperature. The first term of Eq. (1.56) is independent of temperature showing that the second order Doppler shift does not vanish even at \( T=0 \). This is a result of the zero-point motion of the lattice.

The observable second order Doppler shift vanishes if both the temperature and the Debye temperature of source and absorber are equal. This is almost never fulfilled. That is why the total shift of the spectral lines should be called central shift. The isomer shift coming from the Coulomb interaction is only a part (generally the main part) of the central shift. Unfortunately, however, generally the term isomer shift is used for the total shift. Further on we use latter terminology, too.

Similarly to the chemical isomer shift also the second order Doppler shift is pressure-dependent. This pressure-dependence, however, can in most cases be neglected.
1.3.4. QUADRUPOLE SPLITTING

The EFG at the nucleus has two components. First, an EFG is produced by the electrons of the ion concerned while, secondly, the charge distribution of the crystal lattice also contributes to the EFG at the nucleus. An EFG caused by the electrons of its own appears if the ion possesses some electrons of asymmetric charge distribution outside the inner isotropic closed shells. If the local symmetry of the crystal field (i.e. the electrostatic field of the crystal lattice) at the ion is lower than cubic this electrons may cause a considerable EFG.

Instead of $V_{zz}$ and $\eta$ the EFG is often characterized by

$$ q = \frac{V_{zz}}{e} $$

and

$$ \eta q = \frac{V_{xx} - V_{yy}}{e}. $$

The EFG produced by the electrons of the ion ($q_{\text{ion}}$ and $\eta_{\text{ion}} q_{\text{ion}}$) is modified by the shielding of the inner (and originally spherically symmetric) electrons. This is described by Sternheimer's antishielding factor $R_S$ [19]. The EFG of the crystal lattice ($q_{\text{latt}}$ and $\eta_{\text{latt}} q_{\text{latt}}$) is also modified by the same reason; this is characterized by another antishielding factor of Sternheimer $\gamma_{\alpha}$ [19]. For most of the ions $0 < R_S < 1$ while $|\gamma_{\alpha}|$ is often greater than 100.

The EFG at the nucleus is

$$ q = (1 - R_S) q_{\text{ion}} + (1 - \gamma_{\alpha}) q_{\text{latt}} $$

and

$$ \eta q = (1 - R_S) \eta_{\text{ion}} q_{\text{ion}} + (1 - \gamma_{\alpha}) \eta_{\text{latt}} q_{\text{latt}}. $$

The ion contribution (if different from zero) generally exceeds the lattice contribution; the latter, however, is easier to calculate. In point charge approximation the external ions of the lattice are geometrical points at $r_i$ of charge $e_i$. Then, using polar coordinates $(r_i, \theta_i, \varphi_i)$, the lattice EFG we have in the form

$$ q_{\text{latt}} = \frac{1}{e} \sum_i e_i \frac{3 \cos^2 \theta_i - 1}{r_i^3} $$

and

$$ \eta_{\text{latt}} q_{\text{latt}} = \frac{1}{e} \sum_i e_i \frac{3 \sin^2 \theta_i \cos 2 \varphi_i}{r_i^3}. $$

If the coordinates of the ions are known, say, from X-ray diffraction the lattice contribution of the EFG can be calculated if the $e_i$ charges are also known. This involves some difficulties since the ionic charges can only be obtained by MO calculations.

The ionic contribution can be calculated by using the wave functions of the outer electrons. If the wave function of the valence electrons is $\mid \Psi \rangle$ then

$$ q_{\text{ion}} = - \langle \Psi \mid \frac{3 \cos^2 \theta - 1}{r^3} \mid \Psi \rangle $$

(1.64)
and

\[ \eta_{ion} q_{ion} = - \left\langle \Psi \left| \frac{3 \sin^2 \theta \cos 2\varphi}{r^3} \right| \Psi \right\rangle. \]  \hspace{1cm} (1.65)

In the case of hydrogen-like wave functions both Eqs (1.64) and (1.65) are products of an angular and a radial expectation value. The angular part depends on the symmetry of the wave function while the radial part on the radial behaviour of the wave function. The latter which is generally denoted by \( \langle r^{-3} \rangle \) is constant for a free ion. If the ion is chemically bound covalency effects reduce \( \langle r^{-3} \rangle \).

Coming now to the case of iron, the ground state of the Fe\(^{3+}\) ion in weak crystal field is \( ^6S \). The isotropy of this state results in vanishing of the ionic contribution to the EFG. Using Eqs (1.62) and (1.63) we can calculate the lattice contribution in point charge approximation. One obtains relatively small (ca 0.5 mm s\(^{-1}\)) temperature-independent quadrupole splittings.

The ground state of the Fe\(^{2+}\) ion in weak crystal field is \( ^5D \). This 25-fold degenerate state is split by a cubic crystal field without spin-orbit coupling to an orbital doublet \( E_g \) and an orbital triplet \( T_{2g} \). In the most frequent case of octahedral coordination the \( E_g \) states lie by about 1 eV above the \( T_{2g} \) states. Therefore, their contribution to the EFG at room temperature and below can be neglected.

The EFG values induced by the \( ^5D \) states are summarized in Table 1.2.

<table>
<thead>
<tr>
<th>State</th>
<th>( q )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_g ) ( { d_{\pm 3/2} } )</td>
<td>( +(4/7) \langle r^{-3} \rangle )</td>
<td>0</td>
</tr>
<tr>
<td>( d_{\pm 3/2} )</td>
<td>( -(4/7) \langle r^{-3} \rangle )</td>
<td>0</td>
</tr>
<tr>
<td>( T_{2g} ) ( { d_{\pm 3/2} } )</td>
<td>( +(4/7) \langle r^{-3} \rangle )</td>
<td>0</td>
</tr>
<tr>
<td>( d_{\pm 3/2} )</td>
<td>( -(2/7) \langle r^{-3} \rangle )</td>
<td>+3</td>
</tr>
<tr>
<td>( d_{\pm 3/2} )</td>
<td>( -(2/7) \langle r^{-3} \rangle )</td>
<td>-3</td>
</tr>
</tbody>
</table>

In Table 1.2 z axis is chosen to coincide with z axis of the electronic wave-functions, i.e. condition (1.35) has not been used.

If the local symmetry of the nucleus is cubic (which is rarely the case because of the Jahn–Teller effect) the net EFG of the \( T_{2g} \) states is 0. A further axial (e.g. trigonal or tetragonal) perturbing crystal field splits the \( T_{2g} \) level into an orbital doublet and an orbital singlet. If the ground state is singlet then the absolute value of the quadrupole splitting at \( T=0 \) is \( \Delta E_Q = (4/7) \langle r^{-3} \rangle e^2 Q/2 \) according to Eq. (1.42). It is also easy to realize that the absolute value of the quadrupole splitting belonging to any \( T_{2g} \) doublet is \( \Delta E_Q = (2/7) \langle r^{-3} \rangle e^2 Q/2 \). This results in two typical quadrupole splittings for the Fe\(^{2+}\) compounds around 3.6 mm s\(^{-1}\) and 1.8 mm s\(^{-1}\). The latter value occurs more rarely since Jahn–Teller effect is going to split the doublet ground state.

At higher temperatures the EFG of the individual levels is thermally averaged which results in a decrease of the quadrupole splitting. The higher-lying states are mixed to the ground state also quantum mechanically first of all via spin-orbit coupling. This
also leads to a decrease of the quadrupole splitting as compared to the bare splitting \( \Delta E_0 \). A further decrease is caused by the covalency of the chemical bond. This is generally taken into account by an appropriate renormalization of \( \langle r^{-3} \rangle \).

If the local symmetry (point symmetry) is known the quadrupole splitting measured at the nucleus of a Fe\(^{2+} \) ion can be calculated by solving the total \( ^5 \)D problem. This is equivalent to the diagonalization of a 25 \( \times \) 25 complex matrix [20]. In most cases, however, it is sufficient to use \( T_{2g} \) approximation. Then, on one hand, only 15 \( \times \) 15 matrices should be diagonalized and, on the other hand, it can be shown [21] that in this approximation the absolute value of the quadrupole splitting depends only on the energies of the electronic levels and is independent of the point symmetry.

In strong crystal fields the low-spin modifications of Fe ions exist. The ground state of the low-spin Fe\(^{3+} \) ion is \( ^2T_{2g} \) (five of the six \( t_{2g} \) one-electron orbitals are occupied, the \( e_g \) orbitals are empty) while that of the low-spin Fe\(^{2+} \) ion is \( ^1A_{1g} \) (the \( t_{1g} \) orbitals are filled, the \( e_g \) orbitals are empty). That is why the low-spin iron (III) ion resembles the high-spin iron (II) ion while the low-spin iron (II) ion resembles the high-spin iron (III) ion, as far as the quadrupole splitting is concerned.

1.3.5. MAGNETIC HYPERFINE INTERACTION

The magnetic field strength \( H \) at the nucleus consists of many components:

\[
H = H_0 - DM + \frac{4\pi}{3} M + H_s + H_L + H_D
\]

(1.66)

\( H_0 \) is the applied external magnetic field strength. The second term, \(-DM\) is the demagnetization field induced by the magnetization \( M \) of the sample. It should be noted that this form is exact only for an ellipsoid, a principal axis of which is parallel to the external magnetic field. The third term is the so-called Lorentz field. This is caused by the magnetic dipoles of the sample which are far enough from the atom concerned. The field of nearer dipoles (but not of the own atomic electrons) is \( H_d \) which is zero in the case of cubic point symmetry. Sometimes the third and fourth terms together are called Lorentz field.

The second, third and fourth terms of Eq. (1.66) in non-magnetic materials can always be neglected. Even in magnetic substances, their value generally does not exceed \( 1 \) T. The most significant contributions to \( H \) are \( H_s \), \( H_L \) and \( H_D \).

\( H_s \) is the Fermi contact field [22]:

\[
H_s = -\frac{8\pi}{3} \mu_B (|\Psi_1(0)|^2 - |\Psi_0(0)|^2) = -H_C \langle \hat{S} \rangle
\]

(1.67)

Here \( \mu_B \) is the Bohr magneton while \( \Psi_1(\mathbf{r}) \) and \( \Psi_0(\mathbf{r}) \) is the wave-function of the spin-up and spin-down electrons and \( S \) is the atomic spin, respectively. Although only the \( s \) electrons appear with a high probability at the nucleus they are polarized by the non-filled magnetic external shells (e.g. \( 3d, 4f \)). The number of \( s \) electrons is unaffected by this interactions. The radial distribution of the spin-up and spin-down electrons, however, will be different. The polarization is generally only of a few per cents. In
insulators, $H_E$ is roughly proportional to the magnetic moment of the own atom of the nucleus. In metals in addition to the core polarization, other atoms also contribute to the internal field by their magnetic moments via polarization of conduction electrons. $H_L$ is the magnetic field induced by the orbital momentum $L$ of the atom:

$$H_L = -2\mu_B \langle r^{-3} \rangle \langle \hat{L} \rangle = -H_L \langle \hat{L} \rangle,$$  \hfill (1.68)

Finally, $H_D$ is the dipole field induced by the atomic spin $S$:

$$H_D = -2\mu_B \langle r^{-3} \rangle \langle \hat{0}_{SD} \rangle = -H_L \langle \hat{0}_{SD} \rangle,$$  \hfill (1.69)

where $\hat{0}_{SD}$ is the spin dipole operator:

$$\langle \hat{0}_{SD} \rangle = \frac{1}{7I(2I-1)} \sum_k \left[ \frac{3}{2} (\hat{L}_L \hat{L}_k + \hat{L}_k \hat{L}_L) - I(L+1)\delta_{Lk} \right] \hat{S}_k.$$  \hfill (1.70)

1.4. RELAXATION EFFECTS

The shape of the Mössbauer spectrum is substantially influenced by relaxation processes of the atomic electrons. Since Chapter 3 is fully devoted to relaxation phenomena we shall summarize here only their physical bases.

The energy states of a paramagnetic ion are determined by its interaction with the neighbouring ions. As it was shown in Section 1.3 the hyperfine interaction is different in different states of the ion. Since the ion is in thermal equilibrium with its environment it spends a finite time in its stationary states. The transitions between these states are in most cases induced by the interaction of the electron spin with the neighbouring spins (spin-spin relaxation) or with the crystal lattice (spin-lattice relaxation). A significant mechanism of spin-lattice relaxation is the following: the lattice vibrations result in a fluctuating crystal field at the ion which, in turn, influences the expectation value of the electron spin via spin-orbit coupling. This is why for ions of S ground state (e.g. Fe$^{3+}$) the spin-lattice relaxation is slow as compared to the case of ions with a ground state of non-vanishing orbital momentum (e.g. Fe$^{2+}$). The spin-spin relaxation is temperature-independent. It depends, however, markedly on the concentration of paramagnetic ions. In contrast to this, the spin-lattice relaxation depends first of all on temperature.

If the ion spends a long time in every single eigenstate the resultant Mössbauer spectrum will be the superposition of the spectra which can be derived from the hyperfine interactions belonging to the eigenstates. If the transition between the eigenstates is fast the hyperfine interaction is averaged and Mössbauer spectrum shows only the averaged hyperfine interaction. At intermediate transition probabilities complex relaxation spectra can be observed. The transition is taken such as "slow" or "fast". It is slower or faster, respectively, than the characteristic time corresponding to the energy of the hyperfine interaction (the time of a Larmor-precession). Relaxation phenomena can be observed in Mössbauer spectrum if the transition time and the Larmor-time are of the same order of magnitude.

The effect of electron spin relaxation upon Mössbauer spectrum was first discussed by Afanasev and Kagan [23]. They completely solved the problem of one-phonon spin-lattice relaxation processes. The density operator formalism used by them allows, in
principle, exact solution of relaxation problems. Owing to mathematical difficulties exact formulae exist only in certain cases. This fact justifies the application of various semiclassical models for the determination of Mössbauer spectra in the case of relaxation. In these models the fluctuating environment is classically accounted for. This means that the Hamiltonian of the hyperfine interaction is fluctuating statistically among certain discrete values. The parameters of the individual Hamiltonians (hyperfine magnetic fields, EFG's, etc.) and the stochastic matrix of the statistic process (the relaxation times) determine the Mössbauer spectrum. Within the scope of such semiclassical models the most general solution was given by Blume [24]. Wegener [25] elaborated a perturbation theory of the quantum mechanical model in the case of applied (external) magnetic field. A general description independent of the kind of relaxation, however, limited to high frequencies, was given by Afanasev and Gorobchenko [26]. In their phenomenological model the spectrum consists of some shifted and broadened Lorentzians. The phenomenological parameters of the models are contained in a relaxation matrix reflecting the point symmetry of the resonant nucleus.

The various relaxation models are compared in an excellent review of Wegener [27].

1.5. THE INTENSITY OF RESONANCE LINES

1.5.1. BLACKNESS EFFECT

Besides the positions the intensities of the spectral lines also bear significant information concerning the hyperfine interactions. In the following the factors determining the absolute and relative line intensities will be discussed. The intensity is defined as the area of the absorption line of Eq. (1.17). For a Lorentzian shape it has the value

$$I = \frac{\pi A \Gamma_r}{2}$$  \hspace{1cm} (1.71)

where $A$ is the amplitude (height) and $\Gamma_r$ the full width at half maximum (FWHM) of the resonance line.

If both the source and the absorber are thin and neither the source nor the absorbed lines are split by hyperfine interactions then

$$\Gamma_r = 2\Gamma$$  \hspace{1cm} (1.72)

$\Gamma$ being the natural linewidth. Using the data of Table 1.1 in the case of $^{57}$Fe and expressed in velocity units $\Gamma_r = 0.192 \text{ mm s}^{-1}$.

In the case of thick source and/or absorber the shape of the resonance line differs from Lorentzian. When calculating the amplitude and intensity of the resonance line one should take into account that

- the probability of the recoil-free process differs from unity both in the source ($f_s$) and in the absorber ($f_a$).
the gamma-radiation of the resonant transition is weakened by non-resonant atomic absorption both in the source and in the absorber described by absorption coefficients \( \mu_o \) and \( \mu_a \), respectively,

— recoil-free emitted photons may suffer resonant absorption not only in the absorber but also in the source,

— the resonant absorption—just because of its resonant character—cannot be described by an energy-independent mass absorption coefficient. This results in a non-Lorentzian shape of the resonance line in the case of thick source and/or absorber.

If both the source and the absorber possess lines of natural width \( \Gamma \) and of energy \( E_0 \), the transmission (defined as the probability of detecting a photon of the resonant transition behind the absorber) can be given in the following form [28]:

\[
T(v) = e^{-\mu_a \ell_a} \left\{ (1 - f_s) \int_0^\infty \xi(x) e^{-\mu_s x} dx + \frac{f_s \Gamma}{2\pi} \int_{-\infty}^\infty \exp \left[ -f_a v_a \sigma_0 \ell_a' \frac{(\Gamma/2)^2}{(E - E_0)^2 + (\Gamma/2)^2} \right] \right. \\
\times \left. \int_0^\infty \frac{\xi(x)}{[E - E_0(1 + v/c)]^2 + (\Gamma/2)^2} \right. \\
\times \exp \left[ -\left( f_a v_a \sigma_0 \ell_a' \frac{(\Gamma/2)^2}{[E - E_0(1 + v/c)]^2 + (\Gamma/2)^2} + \mu_s \right) x \right] dx \, dE \right\} 
\]  

\[ (1.73) \]

\( v_s \) and \( v_a \) being the number of atoms of the resonant isotope in unit volume of source and absorber, respectively, \( \ell_a \) the thickness of the absorber, \( \xi(x) \) the distribution of emitting nuclei in the source as measured perpendicular to the surface of the source and \( v \) the velocity of the source relative to the absorber.

In the case of a thin source

\[
\xi(x) = \lim_{x' \to +0} \delta(x - x'). 
\]  

\[ (1.74) \]

Substituting Eq. (1.74) into Eq. (1.73) one obtains

\[
T(v) = e^{-\mu_a \ell_a} \left\{ (1 - f_s) + \frac{f_s \Gamma}{2\pi} \int_{-\infty}^\infty \exp \left[ f_a v_a \sigma_0 \ell_a' \frac{(\Gamma/2)^2}{(E - E_0)^2 + (\Gamma/2)^2} \right] \right. \\
\times \left. \frac{1}{[E - E_0(1 + v/c)]^2 + (\Gamma/2)^2} \right\} 
\]  

\[ (1.75) \]

The integral in Eq. (1.75) (the so-called "transmission integral") cannot be given in a closed form. However, the amplitude \( A_T \) and the intensity \( I_T \) of the transmission peak can be expressed as

\[
A_T = \frac{T(\infty) - T(0)}{T(\infty)} = f_s \left[ 1 - \exp \left( -\frac{\lambda_a}{2} \right) I_0 \left( \frac{\lambda_a}{2} \right) \right] 
\]  

\[ (1.76) \]
and

\[ I_T = \int_{-\infty}^{\infty} \frac{T(\infty) - T(v)}{T(\infty)} \, dv = \frac{\pi f_s}{2} \lambda_a \exp \left( -\frac{\lambda_a}{2} \right) \left[ I_0 \left( \frac{\lambda_a}{2} \right) + I_1 \left( \frac{\lambda_a}{2} \right) \right] \]  

(1.77)

where

\[ \lambda_a = v_a f_s \sigma_0 t_a \]  

(1.78)

is the effective thickness of the absorber while \( I_0(y) \) and \( I_1(y) \) are the zeroth and first order Bessel functions of an imaginary argument.

With the provision that \( T(v) \) can be approximated by a Lorentzian to a reasonable accuracy even for high effective thicknesses, in Eqs (1.76) and (1.77) \( \Gamma_r \) can be obtained by the combination of Eqs (1.76), (1.77) and (1.71):

\[ \Gamma_r = \Gamma \frac{\lambda_a \exp \left( -\frac{\lambda_a}{2} \right) \left[ I_0 \left( \frac{\lambda_a}{2} \right) + I_1 \left( \frac{\lambda_a}{2} \right) \right]}{1 - \exp \left( -\frac{\lambda_a}{2} \right) I_0 \left( \frac{\lambda_a}{2} \right)} . \]  

(1.79)

For small effective thicknesses (\( \lambda_a \lesssim 2 \)), \( \Gamma_r \) can be approximated by the first terms of the Taylor expansion of Eq. (1.79):

\[ \Gamma_r \approx \Gamma \left( 2 + \frac{1}{4} \lambda_a + \frac{1}{96} \lambda_a^2 - \frac{1}{64} \lambda_a^3 \right) . \]  

(1.80)

For high effective thicknesses (\( \lambda_a \gtrsim 2 \)) the asymptotic form of the Bessel functions can be used in Eq. (1.79):

\[ \Gamma_r \approx 2 \Gamma \frac{\lambda_a}{\sqrt{\pi \lambda_a - 1}} . \]  

(1.81)

Instead of Eqs (1.80) and (1.81) Visscher's semiempirical expression [7] is often used:

\[ \Gamma_r = \begin{cases} 
\Gamma (2.00 + 0.27 \lambda_a) & \text{if} \quad 0 \leq \lambda_a \leq 5 \\
\Gamma (2.02 + 0.29 \lambda_a - 0.005 \lambda_a^2) & \text{if} \quad 4 \leq \lambda_a \leq 10 
\end{cases} \]  

(1.82)

At high effective thicknesses both \( A_T \) and \( I_T \) can be given in asymptotic forms:

\[ A_T = f_s \left( 1 - \frac{1}{\sqrt{\pi \lambda_a}} \right) , \]  

(1.83)

\[ I_T = \sqrt{\pi} \Gamma f_s \sqrt{\lambda_a} . \]  

(1.84)

If \( \lambda_a \to \infty \), \( A_T \) tends to the saturation value of the \( f \) factor of the source: \( A_T = f_s \). This offers the "black absorber" method for measuring \( f_s \). In contrast to \( A_T \), \( I_T \) is divergent when \( \lambda_a \to \infty \).

Figure 1.7 shows \( A_T, I_T \) and \( \Gamma_r \) as functions of the effective thickness of the absorber \( \lambda_a \). This behaviour is called "blackness effect". Since neither Eq. (1.76) nor Eq. (1.77) is a linear function of \( \lambda_a, f_s \) and \( \lambda_a \) (i.e. \( f_s \)) can be determined by measuring \( A_T \) or \( I_T \) for at least two absorbers of different thicknesses. This way is generally followed when measuring the probability of Møssbauer effect.
Fig. 1.7. Amplitude $A_T$, intensity $I_T$ and width $\Gamma$ of the resonance line as functions of the effective thickness of the absorber $\lambda_a$.

It was supposed above that the measurement is free of background. This is unfortunately never the case. The photons detected behind the absorber originate not only from the transition of interest. A considerable fraction of this background comes from the absorber itself. If the background fraction is denoted by $b$ the measured Mössbauer spectrum becomes

$$N(v) = N(\infty) \left[ (1 - b) \frac{T(v)}{T(\infty)} + b \right]. \quad (1.85)$$

The normalized spectrum defined by Eq. (1.17) is then

$$S(v) = (1 - b) \frac{T(\infty) - T(v)}{T(\infty)}. \quad (1.86)$$

Equation (1.86) compared to Eqs (1.76) and (1.77) leads to the peak amplitude of the normalized spectrum:

$$A_s = (1 - b) A_T. \quad (1.87)$$

The area of the normalized spectrum is then

$$I_s = (1 - b) I_T. \quad (1.88)$$
Equations (1.76) and (1.77) are fulfilled only if the source is thin and both the source and the absorber possess a line of natural width at \( \nu = 0 \). The most essential of these conditions is that the spectrum of the absorber should consist of a single unsplit or of some clearly resolved lines which is rarely the case. A lot of approximations and numerical methods are known to substitute Eqs (1.76) and (1.77) for overlapping Lorentzians. In general case, if polarization effects (see later) can be neglected, instead of Eq. (1.73) for the transmission we have

\[
T(v) = e^{-\mu_0 t_s} \left\{ (1 - f_s) + f_s \int_{-\infty}^{\infty} F \left( E - E_0 \left[ 1 + \frac{\nu}{c} \right] \right) e^{-\frac{\nu \alpha_0 t_s}{c} \sigma(E)} dE \right\}.
\]  
(1.89)

Here \( F(x) \) is the lineshape of the source. For a Lorentzian shape we have

\[
F(x) = \frac{\Gamma}{2\pi} \frac{1}{x^2 + \frac{1}{4} \Gamma^2}.
\]  
(1.90)

It should be mentioned that the meaning of \( T(v) \) and \( f_s \) in Eq. (1.89) is somewhat different from their meaning in Eq. (1.73). The reference in Eq. (1.73) is one elementary gamma-emitting decay within the source while in Eq. (1.89) we refer to one gamma quantum leaving the source. This makes no difference in the further use of \( T(v) \). It is, however, important for the definition of \( f_s \) and \( F(x) \). In fact, in the sense of Eq. (1.89) neither \( f_s \) nor \( F(x) \) can be determined for a given source-material at a given temperature, since the self-absorption within the source appearing explicitly in Eq. (1.73) is now included in \( f_s \) and \( F(x) \). Since the self-absorption is even time-dependent (the source will be enriched in the resonant isotope during the radioactive decay) \( f_s \) and \( F(x) \) should be determined very carefully if one is going to get \( \sigma(E) \) from Eq. (1.89). By the substitution of Eq. (1.89) into Eq. (1.86) the normalized Mössbauer spectrum becomes:

\[
S(v) = (1 - b)f_s \left\{ 1 - \int_{-\infty}^{\infty} F \left( E - E_0 \left[ 1 + \frac{\nu}{c} \right] \right) e^{-\frac{\nu \alpha_0 t_s}{c} \sigma(E)} dE \right\}.
\]  
(1.91)

Equation (1.91) is an integral equation for \( \sigma(E) \) bearing the physical information. Following the method of Ure and Flinn [29], we can, in principle, easily solve it the integral being a convolution. Using velocity units defined by

\[
F_v(v) = F \left( \frac{E_0}{c} \right) \frac{E_0}{c}
\]  
(1.92)

and

\[
\sigma_v(v) = \sigma \left( E_0 \left[ 1 + \frac{\nu}{c} \right] \right)
\]  
(1.93)

one obtains for \( \sigma_v(v) \):

\[
\sigma_v(v) = -\frac{1}{f_s \nu_0 t_s} \ln \mathcal{F}^{-1} \left\{ \frac{1}{\mathcal{F} F_v(v)} \mathcal{F} \left[ 1 - \frac{S(v)}{(1-b)f_s} \right] \right\}
\]  
(1.94)

where \( \mathcal{F} \) is the operator of the Fourier transformation. In practice the application of Eq. (1.94) leads to serious mathematical difficulties because of the inherent statistical
error of $S(\nu)$. To overcome these difficulties a carefully chosen filter-function should be used [29, 30] before the inverse Fourier transformation.

### 1.5.2. ANGULAR DEPENDENCE OF LINE INTENSITIES

If the spectrum is split the intensities and polarizations of the individual lines will have characteristic angular dependence relative to directions determined by the electric and magnetic interactions. In the case of a $1/2 \rightarrow 3/2$ transition and pure axial quadrupole interaction [8]:

\[
I_\pi(\theta) = \frac{3(1 + \cos^2 \theta)}{8} \quad (1.95)
\]

\[
I_\sigma(\theta) = \frac{(5 - 3 \cos^2 \theta)}{8} \quad (1.96)
\]

$I_\pi$ and $I_\sigma$ denoting the intensities of the $\pi(\pm 1/2 \rightarrow \pm 3/2)$ and $\sigma(\pm 1/2 \rightarrow \pm 1/2)$ transitions, respectively, $\theta$ is the angle of the axis of the EFG and the observation direction. The degree of the polarization of the same transitions is [31]:

\[
a_\pi(\theta) = \sin^2 \theta/(1 + \cos^2 \theta), \quad (1.97)
\]

\[
a_\sigma(\theta) = 3 \sin^2 \theta/(5 - 3 \cos^2 \theta). \quad (1.98)
\]

In the case of pure magnetic dipole interaction and $1/2 \rightarrow 3/2$ transition the intensities of the six-line-pattern are [8]:

\[
I_{1,6}(\theta) = \frac{3(1 + \cos^2 \theta)}{16} \quad (1.99)
\]

\[
I_{2,5}(\theta) = \frac{\sin^2 \theta}{4} \quad (1.100)
\]

\[
I_{3,4}(\theta) = \frac{(1 + \cos^2 \theta)}{16} \quad (1.101)
\]

$\theta$ being the angle of magnetic field and observation direction.

In the case of pure electric interaction the intensities of the dipole transition can be given by the quadratic form of an “intensity tensor” $I^h$ [32, 33]:

\[
I^h/(I^h + I^l) = k^0 \cdot I^h \cdot k^0 \quad (1.102)
\]

$I^h$ and $I^l$ being the intensities of the higher and lower energy lines, respectively while $k^0$ is the unity vector parallel to the wave vector of the photon. It can be shown [33] that, for a $1/2 \rightarrow 3/2$ transition, $\text{Tr } I^h = 3/2$.

A general matrix-formalism accounting for the line intensities and polarizations in the case of arbitrary multipolarity of the radiation and arbitrary hyperfine interaction was developed by Spiering [34].

If the crystallites of a polycrystalline sample are randomly oriented the line intensities $I$ can be obtained from the former $I(\theta)$ (or, in the general case $I(\theta, \varphi)$) single crystal or single domain intensities by averaging for the angles:

\[
I = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi I(\theta, \varphi) \sin \theta \, d\theta \, d\varphi. \quad (1.103)
\]
Applying Eq. (1.103) for Eqs (1.95) and (1.96) one obtains
\[ I_\pi = I_\sigma. \]  
(1.104)

Similarly from Eqs (1.99–1.101):
\[ I_{1,6} : I_{2,5} : I_{3,4} = 3 : 2 : 1. \]  
(1.105)

It should be mentioned that Eq. (1.104) holds true generally for pure electric quadrupole interaction and 1/2→3/2 transition. In fact, the macroscopic intensity tensor of a sample with no preferred orientation of the EFG’s should be isotropic. Since the trace of a tensor is invariant under rotation it survives the angular averaging, so it is 3/2. Consequently the macroscopic intensity tensor is
\[ P^b = \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 1/2 \end{pmatrix} \]  
(1.106)
i.e. using Eq. (1.103) \( P^b = 1/2. \)

1.53. **GOLDANSKI–KARYAGIN EFFECT**

It was shown first by Goldanskii, Karyagin and co-workers [35, 36] that the anisotropy of lattice vibrations may result in anomalous line intensities, particularly in an asymmetry of the quadrupole doublet of a polycrystalline sample. In fact, if the point symmetry of an atom is less than cubic its mean-square thermal deviation is different along the different crystallographic directions. It follows then from Eq. (1.11) that in such case the probability of the Mössbauer effect will be also angle dependent. This angular dependence \( f_a(\theta, \varphi) \) should, however, be taken into account in Eq. (1.103). The new expression giving the averaged line intensities is:
\[ I = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi f_a(\theta, \varphi) I(9, \varphi) \sin \theta \, d\theta \, d\varphi \]  
(1.107)
removing the validity of Eqs (1.104) and (1.105).

For the sake of simplicity let us consider a 1/2→3/2 Mössbauer transition and a pure electric quadrupole interaction of axial symmetry. Let us suppose further that the \( f \) factor is also axially symmetric, its symmetry axis coinciding with the EFG axis and that the absorber is thin. The asymmetry of the quadrupole doublet is described [37] by
\[ R_a = \frac{I_\pi}{I_\sigma}. \]  
(1.108)

For an axial point symmetry of the resonant nucleus the angular dependence of the \( f \) factor is given [38] by
\[ f_a(\theta) = \exp \left[ -k^2(\langle z^2 \rangle - \langle x^2 \rangle) \cos^2 \theta - k^2 \langle x^2 \rangle \right] \]  
(1.109)

40
\( \langle z^2 \rangle \) and \( \langle x^* \rangle \) being the mean-square deviations of the resonant nucleus along the \( z \) and \( x \) direction, respectively, \( k \) the wave-vector of the photon and \( \vartheta \) its polar angle. Using Eqs (1.95), (1.96), (1.108), (1.109) and the notation \( \varepsilon_q = k^2 (\langle z^2 \rangle - \langle x^2 \rangle) \), one obtains that

\[
R_q = \frac{\int_0^1 (1 + u^2) e^{-\varepsilon_q u^2} \, du}{\int_0^1 \left( \frac{5}{3} - u^2 \right) e^{-\varepsilon_q u^2} \, du}.
\] (1.110)

The latter equation can be linearized for \(|\varepsilon_q| \leq 1\):

\[
R_q \approx 1 - \frac{2}{15} \varepsilon_q.
\] (1.111)

In the case of pure magnetic dipole interaction the relative line intensities are often described [37] by

\[
R_m = \frac{I_{2, 5}}{I_{3, 4}}.
\] (1.112)

It is easy to realize from Eqs (1.95), (1.96), (1.100), (1.101), (1.107), (1.108) and (1.112) that both \( R_q \) and \( R_m \) depend only on the same integral \( \alpha_q \) of \( f_a(\vartheta) \):

\[
\alpha_q = \int_0^{\pi/2} f_a(\vartheta) \cos^2 \vartheta \sin \vartheta \, d\vartheta
\] (1.113)

\[
R_q = 3(1 + \alpha_q)/(5 - 3 \alpha_q)
\] (1.114)

\[
R_m = 4(1 - \alpha_q)/(1 + \alpha_q)
\] (1.115)

that is

\[
R_m = (3 - R_q)/R_q
\] (1.116)

Equations (1.110) and (1.116) define the line intensities which are expected for anisotropic lattice vibrations in magnetic materials. The same can be used if the quadrupole interaction is small compared to the magnetic one. In any other case \( R_q \) and \( R_m \) can be calculated only numerically.

The appearance of anomalous line intensities in Mössbauer spectra as a result of the anisotropy of lattice vibrations is called Goldanskii–Karyagin effect (GKE).

### 1.54. TEXTURE EFFECTS

Many physical quantities are described by vectors and tensors i.e. by items which can be characterized by a direction or directions. Examples are the hyperfine magnetic field, the crystallographic axes, the EFG tensor, etc. There are two extreme cases which are easy to handle in theoretical calculations:

(i) if the above mentioned directions have a parallel (homogeneous) distribution all over the volume of the sample (e.g. single crystal or single ferromagnetic domain), and

(ii) if these directions have no preferred orientation throughout the sample (e.g. ideal polycrystal or paramagnetic material in zero applied field).
In the strict sense, these extreme cases are very rarely realized in nature. An ideal polycrystal occurs as rarely as an ideal single crystal. Mostly an intermediate case is realized, i.e. the above mentioned directions have some preferred orientation. This is called in the general sense texture. In crystallography texture is a preferred orientation of the crystal axes of the crystallites.

Texture often plays a very important role, particularly in the macroscopic properties of metals. Correspondingly the theory and the standard methods of the texture measurement (mainly with X-ray diffraction) have been worked out in metallurgy [39]. Like in the case of GKE the angular dependence of the Mössbauer line intensities must not be averaged according to Eq. (1.103) for textured samples. Therefore, also texture leads in Mössbauer spectroscopy to anomalous line intensities. It was shown first by Pfannes and Gonser [40, 41] that a relatively small deviation from isotropy in the distribution of crystallographic axes may lead to a considerable asymmetry of 1/2 → 3/2 quadrupole doublets.

To elucidate the effect of texture let us suppose that there is an electric quadrupole interaction of axial symmetry its axis being parallel to the crystallographic c axis with a possible magnetic field also parallel to that axis and that the absorber is thin. We assume further that the texture is also axially symmetric and that the direction of observation is parallel to the texture axis. Finally we suppose that the GKE can be neglected.

The texture in the above case is described [40] by the texture function \( D_{\text{E}}(\theta) \) which is defined so that the probability of finding a c axis between the polar angles \( \theta \) and \( \theta + d\theta \) is \( D_{\text{E}}(\theta) \sin \theta \, d\theta \). Consequently \( D_{\text{E}}(\theta) \) is normalized so that

\[
\int_{0}^{\pi/2} D_{\text{E}}(\theta) \sin \theta \, d\theta = 1.
\]

For an isotropic distribution \( D_{\text{E}}(\theta) \equiv 1 \).

The effect of texture is formally equivalent to the anisotropy of lattice vibrations. The intensity anomaly of the spectral lines is given again by Eqs (1.113–1.116) except that \( f_{a}(\theta) \) should be replaced by \( D_{\text{E}}(\theta) \):

\[
\alpha_{a} = \int_{0}^{\pi/2} D_{\text{E}}(\theta) \cos^{2} \theta \sin \theta \, d\theta.
\]

The above substitution is not quite trivial since \( f_{a}(\theta) \) describes the angular dependence of the resonant fraction in the coordinate system of a crystallite while \( D_{\text{E}}(\theta) \) the distribution of the c axes of the crystallites in the laboratory framework. This difference leads, however, to no difficulty if neither \( f_{a} \) nor \( D_{\text{E}} \) depends on the azimutal angle \( \varphi \). If the direction of observation does not coincide with the texture axis Eq. (1.118) will not hold true any longer. This fact offers a simple possibility to distinguish between GKE and texture. In the case of GKE the observed intensity anomaly does not depend on the position of the absorber relative to the direction of the gamma-rays (except for the trivial change coming from the change of the effective thickness described by Eq. (1.77)). In contrast to this, if the intensity anomaly is caused by texture a rotation of the sample results in an explicit change in the intensity ratios since the texture function is fixed to the sample.
1.6. DIFFUSIONAL BROADENING OF RESONANCE LINES

Atomic motions on a time scale comparable to the nuclear lifetime may lead to a change of the lineshape of the resonance lines. Particularly in glasses diffusion plays an important role. In this chapter we shall discuss the diffusional broadening of resonance lines following the basic paper of Singwi and Sjölander [42].

This general theory of Mössbauer effect only supposes that the nucleus is embedded in some system of atoms. The total Hamiltonian is then

$$\hat{H}_{\text{tot}} = \hat{H} + \hat{H}_{\text{nucl}} + \hat{H}_{\text{rad}} + \hat{H}^* + \hat{K} + \hat{H}_{\text{hf}}$$

(1.119)

Here \(\hat{H}\) is the Hamiltonian of the system of atoms, \(\hat{H}_{\text{nucl}}\) that of the nucleus and \(\hat{H}_{\text{rad}}\) that of the radiation field. \(\hat{H}^*\) is the interaction of the nucleus with the radiation field, \(\hat{K}\) that of the atomic system with the radiation field and \(\hat{H}_{\text{hf}}\) the hyperfine interaction of the nucleus with atoms. If we restrict ourselves to unshifted and unsplit resonance lines and we are not interested in optical transitions the last two terms can be omitted. We shall calculate the cross-section for the absorption of a photon of energy \(E\) and wave vector \(k\).

In Dirac's formalism, the initial state of the atomic system is \(|n_i\rangle\), its final state \(|n_f\rangle\), the initial state of the nucleus \(|A_i\rangle\), its final state \(|A_f\rangle\), the initial state of the radiation field \(|k\rangle\), its final state the vacuum \(|0\rangle\). The energy eigenvalues are defined by

$$\hat{H} |n_i\rangle = \varepsilon_{n_i} |n_i\rangle$$

(1.120)

$$\hat{H} |n_f\rangle = \varepsilon_{n_f} |n_f\rangle$$

(1.121)

$$\hat{H}_{\text{nucl}} |A_i\rangle = E_{A_i} |A_i\rangle$$

(1.122)

$$\hat{H}_{\text{nucl}} |A_f\rangle = E_{A_f} |A_f\rangle$$

(1.123)

$$\hat{H}_{\text{rad}} |k\rangle = E(k) |k\rangle$$

(1.124)

$$\hat{H}_{\text{rad}} |0\rangle = 0$$

(1.125)

The absorption cross-section is given then by Wigner and Weisskopf [43]:

$$\sigma(E) \sim \sum_{n_i, n_f} g_m^i \frac{|\langle n_f, A_f, 0 | \hat{H}^* | k, A_i, n_i \rangle|^2}{(E_0 - E + \varepsilon_{n_f} - \varepsilon_{n_i})^2 + \Gamma^2/4}$$

(1.126)

where \(E_0 = E_{A_i} - E_{A_f}\) and \(\Gamma\) is the natural linewidth of the nuclear transition. \(g_m^i\) is the statistical weight of state \(|n_i\rangle\). The matrix element in Eq. (1.126) can be transformed since

$$\hat{H}^* = \sum_{j,k} C(j, k') \{ \hat{a}_{k'} \exp[ik' r_j] + \hat{a}_{k'}^* \exp[-ik' r_j] \}$$

(1.127)

\(\hat{a}_k\) and \(\hat{a}_k^*\) being the absorption and emission line operators of a photon of wave vector \(k'\), respectively, while \(r_j\) is the coordinate vector of the \(j\)-th nucleon. The \(C(j, k')\) coefficients contain nuclear operators. On denoting the coordinate vector of the center of mass of the nucleus by \(R_A\) relative coordinates can be defined by

$$r_j = R_A + q_j$$

(1.128)
Then
\[
\langle n_t, A_t, 0 | \hat{H} | k, A_1, n_1 \rangle = \langle n_t, A_t | \sum_j C(j, k) \exp[i k \mathbf{R}_A] \exp[i k \mathbf{p}_j] | A_1, n_1 \rangle = 
\]
\[
= \langle n_t | \exp[i k \mathbf{R}_A] | n_1 \rangle \langle A_t | \sum_j C(j, k) \exp[i k \mathbf{p}_j] | A_1 \rangle .
\]
(1.129)

Substituting Eq. (1.129) into Eq. (1.126) and using the same normalization as in Eq. (1.3), we obtain
\[
\sigma(E) = \frac{\sigma_0 \Gamma^2}{4} \sum_{n,t} g_n \frac{|\langle n_t | \exp[i k \mathbf{R}_A] | n_1 \rangle|^2}{(E_0 - E + \epsilon_n - \epsilon_n')^2 + \Gamma^2/4}.
\]
(1.130)

With some algebra, Eq. (1.130) can be brought to the form
\[
\sigma(E) = \frac{\sigma_0 \Gamma}{4 \hbar} \int_{-\infty}^{\infty} \exp[-\frac{i}{\hbar}(E-E_0)t - \frac{\Gamma}{2\hbar} |t|] \langle \exp[-i k \mathbf{R}_A(0)] \exp[i k \mathbf{R}_A(t)] \rangle_T dt.
\]
(1.131)

Here
\[
\mathbf{R}_A(t) = \frac{e^{i \hat{p} t}}{\hbar} \mathbf{R}_A e^{-i \hat{p} t};
\]
(1.132)

while the quantum mechanical and thermal average is denoted by $\langle \ldots \rangle_T$. Equation (1.132) enables us to attribute the meaning “time” to the integration variable $t$ as introduced in Eq. (1.131). Than $\mathbf{R}_A(t)$ is the coordinate operator of the center of mass of the nucleus as used in Heisenberg’s formalism.

Let us calculate the inverse Fourier transform of $\langle e^{-i k \mathbf{R}_A(0)} e^{-i k \mathbf{R}_A(t)} \rangle_T$:
\[
G_s(r, t) = \frac{1}{(2\pi)^3} \int e^{-i k \mathbf{r}} \langle e^{-i k \mathbf{R}_A(0)} e^{-i k \mathbf{R}_A(t)} \rangle_T d^3 k =
\]
\[
= \langle \int \delta[\mathbf{r} + \mathbf{R}_A(0) - \mathbf{r}'] \delta[\mathbf{r}' - \mathbf{R}_A(t)] d^3 r' \rangle_T
\]
(1.133)

In the classical theory, $G_s(r, t)$ describes the correlation of the coordinates of a particle at different instants of time. Consequently, $G_s(r, t)$ is the quantummechanical generalization of the self-correlation function.

Using Eq. (1.131) and the Fourier transform of Eq. (1.133), we obtain:
\[
\sigma(E) = \frac{\sigma_0 \Gamma}{4 \hbar} \int \frac{e^{i k \mathbf{r} - \omega t} - \frac{r}{2 \hbar} |t|}{2 \hbar} G_s(r, t) d^3 r dt,
\]
(1.134)

where $\omega = (E - E_0)/\hbar$. The problem of calculation of the absorption cross-section is reduced thereby to the calculation of $G_s(r, t)$.

The function $G_s(r, t)$ has been calculated by Van Hove [44] for various systems. Particularly for a monoatomic cubic crystal
\[
G_s(r, t) = \frac{e^{-\frac{r^2}{2 \gamma(t)}}}{(2\pi \gamma(t))^{3/2}}
\]
(1.135)

where
\[
\gamma(t) = \frac{\hbar^2}{M} \int_0^\infty \left[ \cosh \left( \frac{v}{2 k_B T} \right) \left( 1 - \cos \frac{vt}{\hbar} \right) - i \sin \frac{vt}{\hbar} \right] \frac{P(v)}{v} dv.
\]
(1.136)
$M$ being the mass of one atom while $P(v)$ the density of states of phonons normalized to unity. Using Eqs (1.134–136), we obtain

$$
\sigma(E) = \frac{\pi \sigma_0 \Gamma}{2} \left[ \frac{1}{2 \pi \left( E - E_0 \right)^2 + \Gamma^2/4} + \sum_{j=1}^{\infty} \frac{\left(2W\right)^j}{j!} g_j(E - E_0, T) \right] e^{-2W} \tag{1.137}
$$

where

$$
g_1(E, T) = \frac{P(|E|)}{2EF(T)} \left[ \frac{E}{2k_B T} \right] \left[ \frac{E}{2k_B T} \right] - 1 \tag{1.138}
$$

$$
g_a(E, T) = \int_{-\infty}^{\infty} g_1(E - E', T) g_{a-1}(E', T) \, dE' \tag{1.139}
$$

$$
\Phi(T) = \int_{0}^{\infty} \frac{P(v)}{v} \left[ \frac{v}{2k_B T} \right] \, dv \tag{1.140}
$$

and

$$
2W = \frac{h^2 k^2}{2M} \Phi(T) \tag{1.141}
$$

The cross-section as given by Eq. (1.137) consists of two terms. The first term describes a sharp absorption line at $E = E_0$ of natural width; this is Mössbauer's recoil-free resonance line. The second term (the sum) describes the transitions involving a change of the phonon-state. The factor $e^{-2W}$ can easily be identified as the Debye–Waller factor $f$ as introduced in Section 1.2.

In the Debye approximation

$$
P(v) = \begin{cases} 
\frac{3v^2}{(k_B \theta_D)^2} & \text{if } v \leq k_B \theta_D \\
0 & \text{otherwise}
\end{cases} \tag{1.142}
$$

Combining Eqs (1.140–142) and Eq. (1.6), we obtain Eq. (1.12).

The diffusion of atoms in a solid will be described in terms of a jump model. Let us denote the mean time which an atom spends in a certain site before jumping to another one by $\tau_0$. Assuming that the jumps are governed by a Markov process. Singwi and Sjölander [42] calculated the appropriate self-correlation function, which, replacing Eq. (1.134) gives

$$
\sigma(E) = \frac{\sigma_0 \Gamma}{4} \left[ \frac{\Gamma + (2h/\tau_0)[1 - \alpha(k)]}{(E - E_0)^2 + \left[ (\Gamma + (2h/\tau_0)(1 - \alpha(k)))^2/4 \right]} + \text{phonon terms} \right] e^{-2W}, \tag{1.143}
$$

where

$$
\alpha(k) = \int e^{ikr} \, h(r) \, d^2 r \tag{1.144}
$$

$h(r)$ being the probability density of finding an atom after one jump at a distance $r$ from the origin of the jump.

Equation (1.143) shows that a diffusive motion of resonant nuclei results in a
broadening of the Mössbauer line

\[
\Delta \Gamma = \frac{2h}{\tau_0} \left[ 1 - \int e^{ikr} h(r) \, d^3r \right].
\] (1.145)

To estimate the line broadening let us suppose that the jump takes place along any edge of a cube with a probability 1/6. If the interatomic spacing is \( l \), the diffusion coefficient defined by

\[
D = \frac{1}{6\tau_0} \int r^2 h(r) \, d^3r
\] (1.146)

is

\[
D = \frac{l^2}{6\tau_0}.
\] (1.147)

Since in practical cases the integral in Eq. (1.145) is much less then unity, a rough estimate of the diffusion constant from the line broadening is given by

\[
D = \frac{l^2}{12h} \Delta \Gamma.
\] (1.148)

1.7. EXPERIMENTAL TECHNIQUES

1.7.1. SPECTROMETERS

The Mössbauer spectrum is measured by scanning the absorption cross-section vs. energy. As it was shown in Section 1.2 this can be done by moving the source with velocities of several mm s\(^{-1}\) relative to the absorber. In the first years of Mössbauer spectroscopy this was realized with the help of various mechanical and hydraulic systems. With the appearance of electrodynamic drives the latter method became exclusive.

An electrodynamic drive (Fig. 1.8) consists of two electrodynamic loudspeakers. One coil is used, like in the loudspeaker, to generate motion while the other to measure the actual velocity. The latter is used to be fed back to a differential amplifier connected to a velocity generator.

![Fig. 1.8. Electrodynamic drive](image)
Photons passing through the absorber are registered with scintillation or proportional counters. Scintillation counters have higher efficiency and less dead time. In contrast to proportional counters they also detect high energy (≥ 60 keV) photons which may overload the amplifier. To avoid this, very thin (0.1–0.2 mm) NaI(Tl) scintillation crystals are used. The advantage of proportional counters is the higher resolution and their insensitivity to external magnetic fields. The pulses belonging to the Mössbauer transition are selected by a single-channel analyzer. If this cannot be done because some other γ- or X-ray lines overlap with the Mössbauer line semiconductor detectors or special filters are used.

![Diagram](image)

*Fig. 1.9. Block scheme of a Mössbauer spectrometer*

Up-to-date spectrometers are generally operating in the variable velocity regime. The whole velocity range of interest is scanned many (typically 10 to 50) times per second. The counts detected behind the absorber and selected by the single-channel analyzer are stored in a memory (mostly in the memory of a multichannel analyzer) at an address corresponding to the instantaneous velocity of the source. The memory contains therefore at any time the whole spectrum collected since the start of the measurement. The block scheme of a spectrometer is shown in Fig. 1.9.

An overwhelming majority of Mössbauer spectrometers is operating in the above described "multiscaling regime". The previously used "pulse height modulation regime" [7] is used only to fulfill special requirements.

An undistorted spectrum in the memory of the spectrometer can only be expected if the velocity is a linear function of time [Fig. 1.10(a)]. It is not always easy to realize such a law of motion especially if the velocity is high or the mass to be moved is large. Many spectrometers use a sinusoidal law of motion [Fig. 1.10(b)] to avoid these difficulties. To convert the stored spectrum to linear form mostly numerical methods are used.

Many spectrometers are controlled by small computers or microprocessors. These spectrometers are able not only to control the measurement but also to perform some
Fig. 1.10. Relative velocity of source and absorber as a function of time in the case of (a) constant acceleration and (b) sinusoidal regime.

Evaluation of the spectrum (addition, correction or stripping of spectra, fitting them with a number of parameters, linearizing the sinusoidal wave-form, etc.).

If the actual velocity is relatively far from the ideal one or if a high accuracy of the velocity scale is necessary, additional velocity-measuring devices like laser interferometers are used.

Since many types of Mössbauer spectrometers are commercially available we do not go into further technical details here.

Further equipment is necessary to set the temperature of the sample and/or to apply a magnetic field. Above room temperature electric furnaces are used. These are mostly vacuum furnaces to prevent the sample from oxidization. The requirements for the vacuum system are not high: a minimum pressure of $10^{-3}$ Pa is sufficient. If transformation kinetics are to be studied furnaces of small heat capacity but of high stability should be preferably used.

Below room temperature cryostats cooled with liquid nitrogen, liquid helium or sometimes with dry ice are used. Cryostats (especially exchange gas cryostats) and furnaces are often combined into one unit. This cannot be done with helium-cooled immersion cryostats which are often supplied with superconducting magnets. In such cryostats the movement of the drive is generally transduced to the source by a long rod of about 100 g mass. This results in difficulties with the proper linear velocity waveform as described above.

Since many kinds of cryostats are commercially available one should be careful when choosing the appropriate one for a certain purpose. Many cryostats are, for example, not suitable for studying frozen aqueous solutions since it is impossible to put the pre-cooled sample into the holder so that it does not reach its glass transition temperature which is for such systems at about 160 K.

To apply magnetic fields up to about 1.5 T conventional electromagnets are used. Above this value superconducting magnets are applied. When using magnetic fields
one should check if the scattered magnetic field does not affect the drive and/or the
detector. On the other hand, in some special cases (e.g. dilute Fe$^{3+}$ systems) the sample
should be shielded even against the scattered field of the drive because magnetic fields
as low as $10^{-2}$ T may change the Mössbauer spectrum.

Sources in conventional Mössbauer spectroscopy should have an unsplit and
unbroadened line. Moreover, their recoil-less fraction should be as high as possible. In
$^{57}$Fe spectroscopy this is generally realized by diffusing electrolyzed $^{57}$Co into
paramagnetic metals or alloys such as stainless steel, Cr, Pd, Cu, Rh, etc. The two latter
hosts are very advantageous because of their narrow line even at 4.2 K. Moreover, they
are rather insensitive to scattered magnetic fields at this temperature since the external
field is practically cancelled by the induced one. In $^{119}$Sn spectroscopy the most
suitable source is Ba$^{119m}$SnO$_3$. A great variety of long-lived Mössbauer sources is
commercially available.

The standard geometry of Mössbauer spectroscopy is transmission. It is possible
and sometimes even useful, however, to detect scattered resonant photons or X-rays,
conversion or Auger electrons associated with the resonant scattering process. Gammas
and X-rays bring information on the state of an about 100 µm thick surface
layer. This is, in a microscopic sense, the bulk rather than the surface. The importance
of this geometry is that it makes possible the non-destructive study of bulk samples.

When detecting electrons a much thinner surface film (ca 100 nm) is seen. Electrons
with an energy of about 10 keV are stopped inside the material when coming from
deeper. This technique called Conversion Electron Mössbauer Spectroscopy (CEMS)
is generally realized by using the sample as the cathode of a flow-gas proportional
counter. The efficiency is enhanced here by the internal conversion coefficient $\alpha$ being
8.9 for $^{57}$Fe. Because of the increasing importance of surface studies of implanted
systems, corrosion products, catalysts, etc. CEMS is getting more and more standard
technique shown by the fact that CEMS detectors are produced commercially.

1.7.2. ESTIMATION OF OPTIMUM ABSORBER THICKNESS

If the activity of the source and/or the concentration of resonant nuclei in the absorber
is low, Mössbauer lines of appropriate intensity can be produced only with long
running times. In such cases it is advisable to estimate the optimum absorber thickness
yielding the maximum information per unit of running time.

As it was shown in Section 1.5.1 [cf. Eq. (1.73)] an increase in the layer thickness for a
sample of given composition is accompanied by an increase not only of the number of
resonant nuclei in the path of the radiation, and hence of the extent of nuclear
resonance absorption but also of the non-resonant atomic absorption originating from
the shell electrons of all atoms in the sample. An increase in the absorber thickness
therefore results in two opposing effects, and it is thus to be expected that (as regards the
measurement) there will be an optimum thickness of the absorber.

A number of methods have been developed to determine this layer thickness [45–
49]. One of these methods [47, 49] will be described here in detail. The optimum layer
thickness is that one for which the shortest time is needed to perform a measurement so
that the relative size of the measured effect is greater than a prescribed $\beta$ times the
relative standard statistical deviation of the baseline, i.e. using the notations of Sections
1.2 and 1.5.1:

$$A_s > \frac{\beta}{\sqrt{N(\infty)}}. \quad (1.149)$$

Here and later on in this chapter it is supposed that, for the sake of simplicity, both
the emission and the absorption spectrum consist of single lines of Lorentzian shape
and of the same width.

Combining Eqs (1.87) and (1.149), we obtain

$$(1 - b)^2 N(\infty) A_1^2 > \beta^2. \quad (1.150)$$

To determine the optimum layer thickness $t_{opt}$ let us assume that the total time of the
measurement is $t_m$ using a multichannel analyzer of $G$ channels. Pulses are thus
collected in one channel for a time $t_m/G$ assuming that they are fed into each channel for
the same time. The number of pulses without background collected by one channel
during the whole measurement is

$$N(v) - bN(\infty) = I_x(v) \frac{t_m}{G}; \quad (1.151)$$

where $I_x(v)$ is the background-free intensity of detected pulses at source velocity $v$.

At non-resonant velocities only the atomic absorption needs to be considered:

$$I_x(\infty) = I' e^{-\mu_a t_a}. \quad (1.152)$$

The absorption coefficient $\mu_a$ in Eq. (1.152) refers to the absorption of the Mössbauer
line and does not contain the attenuation of the background radiation which also
depends on the layer thickness $t_a$.

Let us introduce the dimensionless layer thickness by

$$z = \mu_a t_a. \quad (1.153)$$

With this notation, Eqs (1.151) and (1.152) give

$$(1 - b) N(\infty) = I' e^{-z} \frac{t_m}{G}. \quad (1.154)$$

If the intensity of the background detected behind the absorber of dimensionless
thickness $z$ is denoted by $I_b(z)$ then the number of background pulses collected in one
channel during the entire measurement time is

$$bN(\infty) = I_b(z) \frac{t_m}{G}. \quad (1.155)$$

Adding Eqs (1.154) and (1.155), we obtain the equation:

$$N(\infty) = [I' e^{-z} + I_b(z)] \frac{t_m}{G}. \quad (1.156)$$
and taking square of Eq. (1.154) and dividing it by Eq. (1.156):

\[(1 - b)^2 N(\infty) = \frac{I' e^{-z}}{G \left[ 1 + \frac{I_b(z)}{I'} e^z \right]} t_m. \tag{1.157}\]

Substituting Eq. (1.157) into inequality (1.150) and expressing the minimum necessary measurement time, we arrive at:

\[t_m^{\text{min}} = \left[ 1 + \frac{I_b(z)}{I'} e^z \right] \frac{G \beta^2}{I' A_T^2} e^z. \tag{1.158}\]

Substituting the expression for \(A_T\) from Eq. (1.76) into Eq. (1.158) and introducing the dimensionless resonant nucleus concentration

\[\gamma = \frac{\lambda_0}{2z}, \tag{1.159}\]

one obtains

\[t_m^{\text{min}} = \frac{G \beta^2}{I' f_s^2} \left[ 1 + g(z) e^z \right] \frac{e^z}{\left[ 1 - e^{-\gamma z} I_0(\gamma z) \right]^2} \tag{1.160}\]

where the \(g(z)\) background ratio is defined by

\[g(z) = \frac{I_b(z)}{I'}. \tag{1.161}\]

If \(\beta\) is fixed and only the effect of the layer thickness is examined, then instead of Eq. (1.160) it is sufficient to consider its thickness-dependent factor, i.e.

\[T(z, \gamma) = \left[ 1 + g(z) e^z \right] \frac{e^z}{\left[ 1 - e^{-\gamma z} I_0(\gamma z) \right]^2}. \tag{1.162}\]

Figure 1.11 shows \(T(z, \gamma)\) for \(b = 0\), i.e. when the background is negligible \((g(z) = 0)\). At low values of \(\gamma\) the minimum for \(z\) is fairly sharp, and in such a situation, therefore, it is particularly important to maintain the optimum layer thickness. The latter can be calculated by solving the transcendent equation

\[\frac{dT}{dz} = 0. \tag{1.163}\]

Figure 1.12 presents the calculated \(z_{\text{opt}}(\gamma)\) function for a negligible background. With decreasing \(\gamma\), the optimal value of \(z_{\text{opt}}\) tends towards 2. For low values of \(\gamma\) where optimization is most essential the optimum layer thickness is approximately constant and equal to the limiting value

\[\xi = \lim_{\gamma \to 0} z_{\text{opt}}(\gamma). \tag{1.164}\]

In general case when \(b \neq 0\), \(\xi\) may differ from 2 and is given by the solution of the following equation:

\[\xi = \frac{2}{1 + \frac{g(\xi) + g'(\xi)}{g(\xi) + e^{-\xi}}} \tag{1.165}\]
Fig. 1.11. Time factor function $T(z, \gamma)$ of the minimum measurement time plotted against the dimensionless absorber thickness $z$

Fig. 1.12. The optimum dimensionless absorber thickness $z_{opt}$ as a function of the dimensionless resonant nucleus concentration $\gamma$
where
\[ g'(\xi) = \frac{dg}{dz} \bigg|_{z=\xi} \quad (1.166) \]

In general, it is difficult to take the background into consideration in the calculation of \( \xi \) from Eq. (1.165), since it is necessary to know the course of \( g(z) \). In many cases (e.g. in most \(^{57}\text{Fe} \) measurements), however, the background ratio practically does not depend on \( z \), hence \( g'(z) \approx 0 \) and \( g(z) = g_0 \) (constant). Equation (1.165) can then be easily solved. The solution is shown in Fig. 1.13. With increasing \( g_0 \), \( \xi \) decreases from 2 and asymptotically approaches unity. For a background greater than 50\% \( (g_0 > 1) \) \( \xi = 1 \) can be taken as a good approximation.

In general case when \( g'(z) \neq 0 \), the condition for optimum thickness can be given, as well. In this case even \( \xi > 2 \) may occur.

From a practical aspect, it is important to know how well the value of \( \xi \) (readily obtained from the background ratio) replaces \( z_{\text{opt}} \) which also depends on \( \gamma \). Figure 1.14 shows the optimum time factor \( T(z_{\text{opt}}(\gamma), \gamma) \) and the approximate optimum time factor \( T(\xi, \gamma) \) for the background-free case. The two curves start to diverge significantly at \( \gamma \) values for which \( T \) is fairly small. The exact meaning of this result as regards time depends on the concrete values of the other parameters in Eq. (1.160). In general, it is a short time. Furthermore, frequently an unrealistically high concentration of resonant nuclei would correspond to such a high value of \( \gamma \).

The optimum layer thickness has a very simple approximate form if the background
ratio does not depend on the layer thickness and is greater than ca 50%. Then, $\xi \approx 1$ and, from Eq. (1.153):

$$t'_{opt} = \frac{Z_{opt}}{\mu_a} \approx \frac{\xi}{\mu_a} \approx \frac{1}{\mu_a}$$  \hspace{1cm} (1.167)

### 1.8. EVALUATION OF MÖSSBAUER SPECTRA

#### 1.8.1. SPECTRUM FITTING

The evaluation of a Mössbauer spectrum means the determination of physical parameters (e.g. isomer shift, quadrupole splitting, magnetic field strength, peak amplitudes and widths) from the spectrum. This makes no difficulty if the spectrum consists of a few clearly resolved lines. In such cases the parameters can be extracted directly from the spectrum although their correct determination can hardly be performed without computer programs.

More complex spectra can only be evaluated with computer algorithms. This can be done by fitting a function of certain parameters to the spectrum. The fitting is generally made by using the least squares method, i.e. by minimizing

$$\chi^2 = \sum_{i=1}^{G} \frac{1}{N_i} \left[ N_i - \tilde{f}^i(b_1, b_2, \ldots, b_{p_n}) \right]^2$$  \hspace{1cm} (1.168)

for the parameters $b_1, b_2, \ldots, b_{p_n}$. Here $N_i$ is the total number of counts in the $i$-th channel, $\tilde{f}^i(b_1, b_2, \ldots, b_{p_n})$ is the value of the model function in the $i$-th channel and $G$ is the total number of channels.
If the absorber is not too thick the spectrum is a sum of Lorentzians of negative amplitudes superimposed to a base line:

$$\tilde{f}^i = B - \sum_{j=1}^{p} \frac{\Gamma_j^2}{4} \frac{A_j}{(\nu - \delta_j)^2 + \Gamma_j^2/4}.$$  \hfill (1.169)

The way of evaluation, however, even in this case is not quite trivial. Since Lorentzians have rather long “tails”, different peaks of a spectrum can rarely be fitted independently of each other. Simultaneous fitting of \(p\) peaks is an iteration process for \(p_a = 3p + 1\) parameters. This is equivalent to the calculation and inversion of a matrix of order \(p^2\) in each iteration step, if Newton’s method [50] for minimizing \(\chi^2\) of Eq. (1.168) with \(f^i\) of Eq. (1.169) is used. In most cases, however, only a few of these parameters are independent. The spectrum of an ideal \(^{57}\text{Fe}\) magnetic sextett of a powder sample depends only on base line, amplitude, magnetic field, quadrupole splitting, isomer shift and linewidth i.e. on 6 parameters rather than on \(3 \times 6 + 1 = 19\).

The number of independent parameters should be decreased in some other cases, too. With physical reasoning, especially in the case of spectra of poor statistics, some parameters should be fixed or should be chosen to be equal to some other parameters or some other constraints should be applied. A new constraint is equivalent to a new model function which should be used in Eq. (1.168) instead of \(\tilde{f}^i\) defined by Eq. (1.169). The most straightforward way of minimizing \(\chi^2\) is to write a new program or at least a new subroutine for every new model function. This method was used at the early stage of Mössbauer spectroscopy. Later on it was realized [51] that a great deal of constraints can be handled with the same fitting program. In fact, the majority of constraints being applied during the evaluation of thin absorber spectra can be described as inhomogenous linear transformation of the parameters \(B, A_j, \delta_j, \Gamma_j\) \((j = 1, 2, \ldots, p)\). These “peak-parameters” are unified in a \(p_a\)-dimensional vector \(a\) while the independent physical parameters in a \(p_b\)-dimensional vector \(b\). Of course, \(p_b \leq p_a\).

The inhomogeneous linear transformation connecting \(a\) to \(b\) is:

$$a_j = \sum_{k=1}^{p_b} t_{jk} b_k + c_j,$$  \hfill (1.170)

the matrix elements \(t_{jk}\) and the vector elements \(c_j\) being constants. Every constraint is described by matrix \(T\) and vector \(c\). The model function can be expressed both in terms of \(a\) and \(b\):

$$f^i(a) = \tilde{f}^i(b)$$  \hfill (1.171)

The result of the evaluation should be vector \(b\). During the numerical calculation one should use therefore \(\tilde{f}^i(b)\) and \(\partial f^i/\partial b_k\) since minimization procedures generally need the derivatives of the model function. Using Eq. (1.170) both \(\tilde{f}^i(b)\) and \(\partial f^i/\partial b_k\) can be expressed in terms of \(f^i(a)\) and \(\partial f^i/\partial a_j\):

$$\tilde{f}^i(b) = f^i(a) = f^i(Tb + c)$$  \hfill (1.172)

and

$$\frac{\partial \tilde{f}^i}{\partial b_k} = \sum_{j=1}^{p_a} \frac{\partial f^i}{\partial a_j} \bigg|_{a = Tb + c} t_{jk}.$$  \hfill (1.173)
The whole iteration procedure can be performed in the space of \( b \) by the use of Eqs (1.172) and (1.173). Since \( b \) contains the physical parameters, the above method directly yields their values, errors and covariance.

There are cases (e.g. thick absorber, electron spin relaxation with medium frequencies) when the model function cannot be given in the form of Eq.(1.169). In some other cases (e.g. combined hyperfine interaction, spectra measured in an applied magnetic field and described in terms of spin Hamiltonian or ligand field parameters) the peak-parameters cannot be given in the form of Eq. (1.170). Then, of course, the above method does not work. The only way of solving the problem is to return to the method of “one function–one program”. Up-to-date computers enable us, however, to incorporate many model functions into one large program. In fact, a very versatile program developed by Müller [52] takes the advantages of both described methods by incorporating a lot of subroutines each describing a different theory and by using the method of transformation matrices for applying constraints.

Minimizing \( \chi^2 \) one is often faced with the problem of poor convergency. The reason for such behaviour is that the minimum of \( \chi^2 \) as a function of some parameters or of certain combination of some parameters is very “flat”. There exist mathematical methods (e.g. [53]) which are convergent even in such “ill-conditioned” cases. At this point, however, a warning should be made. The application of such methods brings one rarely closer to the solution of the physical problem. The above situation means namely that the extraction of more information from the spectrum was attempted than it in fact contains. The solution of the problem is consequently not assuring artificially the convergency but (of course using additional information) decreasing the number of free parameters by applying some constraints.

1.8.2. EVALUATION OF FIELD DISTRIBUTIONS

Mössbauer spectra of non-crystalline solids often consist of broad non-Lorentzian lines. The reason for this fact is a distribution of the parameters of the hyperfine interactions as a result of the non-uniformity of the local environments. To fit such spectra one should construct a model function for the distribution of hyperfine interactions depending on a few parameters. The latter parameters should be adjusted so that the minimum of \( \chi^2 \) is obtained. To construct a reliable distribution function with good physical arguments is, unfortunately, rather difficult.

Another approach of the evaluation of such spectra is the direct determination of the distribution function from the spectrum. If the problem is one-dimensional, e.g. if only the hyperfine magnetic field has a distribution, the distribution function, at least in principle, can be readily obtained. The probability of the absorption at velocity \( v \) for a thin absorber is

\[
S(v) = \int_{-\infty}^{\infty} P_d(v') L_s(v-v') \, dv',
\]

(1.174)

\( P_d(v) \) being the distribution function to be determined and \( L_s(v) \) the shape of a spectral line without broadening. Equation (1.174) says that \( S \) is the convolution of \( P_d \) and \( L_s \). Consequently, denoting the Fourier transforms of \( S \), \( P_d \) and \( L_s \) by \( s \), \( p_d \) and \( l_s \),

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respectively:

\[ s(k) = p_d(k) I_s(k), \]  

the \( k \) frequency being the variable of the Fourier transformation. Now \( P_d(v) \) can readily be obtained:

\[ P_d(v) = \mathcal{F}^{-1} \frac{s(k)}{I_s(k)} = \mathcal{F}^{-1} \frac{\mathcal{F} S(v)}{\mathcal{F} L_\sigma(v)} \]  

\( \mathcal{F} \) representing the Fourier transformation. If, e.g.,

\[ L_\sigma(v) = \frac{\Gamma}{\pi} \frac{1}{v^2 + \Gamma^2}, \]  
i.e. a zero-centred Lorentzian of \( 2\Gamma \) width then

\[ I_s(k) = e^{-|k|\Gamma}. \]  

In practice, the solution of integral equation (1.174) is not very easy. Unfortunately, the spectrum and consequently the absorption \( S \) can only be measured with a finite statistical error. A direct application of Eq. (1.176) would largely enhance the high frequency part of the error. To overcome this difficulty a filter function \( d(k) \) is used. Before the inverse Fourier transformation \( s(k)/I_s(k) \) is multiplied by \( d(k) \). If \( d(k) \) is low enough at high frequencies the statistical error is strongly damped. On the other hand, the multiplication by the filter function modifies the lineshape and leads in the case of a sharp cut-off frequency of the filter function to false (so-called Gibbs) oscillation of \( P_d(v) \) [54]. Therefore the shape of \( d(k) \) should be chosen with special care. The parameters of \( d(k) \) should be determined so that the Gibbs oscillations do not overcome the error of \( P_d(v) \). In Mössbauer spectroscopy the filter functions

\[ d(k) = \exp\left(-k^2/2\sigma_d^2\right) \]  

and

\[ d(k) = \frac{1}{\exp \left[(k-k_0)\Gamma \right] + 1} \]  

have been applied with some success [29], [30].

Window’s method [55] is closely related to the above Fourier technique. In this procedure the numerical Fourier transformation is replaced by fitting a finite trigonometric series to the spectrum with the least squares method. Another fitting process to determine \( P_d(v) \) was suggested by Hesse and Rübertsch [56]. In their method the convolution integral of Eq. (1.174) is replaced by a sum and the values of \( P_d(v) \) at discrete points are fitting parameters. This procedure gives thereby directly the distribution function at a finite number of points.

The distribution function of hyperfine interactions in non-crystalline (or just disordered) solids is mostly two-, three- or even more-dimensional. In fact, if an unbrodened spectrum \( L_\sigma(v, \delta, \epsilon, H) \) depends only on the isomer shift \( \delta \), the quadrupole splitting \( \epsilon \) as defined by Eq. (1.51) and on the magnetic field strengths \( H \) then Eq. (1.174) should be replaced by

\[ S(v) = \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty P_d(\delta, \epsilon, H) L_\sigma(v, \delta, \epsilon, H) \, d\delta \, d\epsilon \, dH. \]  

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Since \( L_a(v, \delta, \varepsilon, H) \) is known the integral equation (1.181) can be, in principle, solved again. Unfortunately, the mathematical difficulties are now even much greater than before. Levitz et al. [57] succeeded in solving the two-dimensional problem by generalizing the method of Hesse and Rübertsch [56]. Their algorithm is very useful when paramagnetic glasses are concerned.

All these methods (Window [55], Hesse and Rübertsch [56], Levitz et al. [57]) are closely related to the Fourier technique. It is no wonder, therefore, that they are very sensitive to proper choice of their internal parameters like the number of terms in the trigonometric series in Window's procedure. If this is not properly done the obtained distribution functions may contain some false peaks similar to the Gibbs oscillations. The inadequate use of the procedures of Window [55] and of Hesse and Rübertsch [56] already led to many controversies particularly as concerning the hyperfine field distribution in ferromagnetic metallic glasses.

An idea of Vincze [58] may bring in some cases closer to the solution of integral Eq. (1.181). This author suggests to get more information regarding \( P_d(\delta, \varepsilon, H) \) by measuring the spectra of ferromagnetic glasses at different angles relative to the direction of the magnetization. The samples in this case are magnetized to saturation with a small external magnetic field. By changing the angle of observation one changes the relative line intensities of \( L_a(v, \delta, \varepsilon, H) \) but not their line positions. Particularly it is possible therefore to construct two linear combinations of two spectra measured at different angles so that the first contains only the 1st, 3rd, 4th and 6th lines while the second one the 2nd and 5th lines of the original spectra. If the procedure of Levitz et al. [57] is applied for the latter linear combination a two-dimensional projection of \( P_d(\delta, \varepsilon, H) \), namely the simultaneous distribution of \( \delta - \varepsilon \) and \( H \) is obtained.
43. Weisskopf, V. and Wigner, E., Z. Physik 63, 54 (1930); ibid 65, 18 (1930).