

## *The Electric Field Gradient and the Quadrupole Interaction*

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The Mössbauer effect has become a popular method in analytical chemistry. In contrast to other techniques such as x-ray spectroscopy, NMR, EPR, and MCD where highly sophisticated evaluation procedures are applied to obtain reliable information on the chemical compound, the Mössbauer effect is generally used on a low level concerning the evaluation of quadrupole split spectra. This procedure on a low level is favored by the structure of the spectra especially the simple doublet of the  $3/2 \rightarrow 1/2$  nuclear transitions in paramagnetic and diamagnetic compounds. The separation of the two absorption lines, the quadrupole splitting  $\Delta E_Q$ , and the center of the two lines, the isomer shift, are easily derived from the spectra. To obtain these two parameters, which comprise already a lot of chemical information, there is no need of a complete theory. Further information from the quadrupole split spectra is given by the sign and the asymmetry of the electric field gradient tensor at the nucleus and its orientation with respect to the crystal axes. The evaluation of these parameters from the Mössbauer spectra requires already a relatively complicated theory which is only available in original publications.<sup>1-3</sup> The situation is made even more difficult by the matter of fact that in most cases the tensor components cannot be uniquely measured; rather, only interrelations between them are obtained from the measured quantities of the spectra.<sup>4</sup> A further complication is introduced by an anisotropic vibrational amplitude of the Mössbauer atom which gives rise to an anisotropic Debye-Waller factor. These points prevented a general application of all possibilities of the Mössbauer effect, although very nice work

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had been done on sodium nitroprusside<sup>5</sup> and on the heme group of deoxymyoglobin<sup>6</sup> and on CO-liganded myoglobin<sup>7</sup> where the difficulties concerning the preparation of sufficiently large single crystals enriched in  $^{57}\text{Fe}$  had to be overcome. On the other hand the calculation of the electric field gradient in molecular crystals by molecular orbital (MO) approaches has been improved very much,<sup>8</sup> so that a comparison with detailed experimental data has become desirable. It seems therefore to be justified to present in detail the mathematical tool for the evaluation of the quadrupole split Mössbauer spectra.

In the last years several simplifications of the theoretical description of the intensities of the Mössbauer absorption lines have been introduced.<sup>9-11</sup> All of these descriptions have in common that the intensities are calculated by the use of tensors of different rank according to the multipolarity of the nuclear transition. This concept is standard method in the evaluation of perturbed angular correlation (PAC) experiments.<sup>12</sup> The different types of Mössbauer absorbers are single crystals and random and textured<sup>13,14</sup> powders; these require a generalization of the theory which incorporates the distribution function of the orientations of the principal axes systems of the EFG tensors in the absorber. This has been done for the dipole transition in Mössbauer experiments<sup>15</sup> and very recently for PAC experiments.<sup>16</sup> The case of a random powder and an anisotropic Debye-Waller factor which leads to the Goldanskii-Karyagin effect<sup>17,18</sup> has also been reconsidered by the tensor concept.<sup>15</sup>

This chapter tries to make the reader familiar with the tensor concept. It has been used throughout and has been extended also to mixed transitions ( $M1/E2$ ). Both the texture function and the anisotropic Debye-Waller factor are included in the theory. A concise description of this complicated situation is achieved by the introduction of "super-texture" components. The chapter is divided into five sections. The first three are more theoretical: they introduce the equations required for the last two sections, which deal with the application of the theory. We start with the nuclear spin Hamiltonian of the quadrupole interaction and some properties of the electric field gradient in Section 1. In the second section the line positions of the Mössbauer transitions are considered for several nuclei which have been selected to demonstrate the application of the theory. These are the ( $3/2^- \rightarrow 1/2^-$ ) magnetic dipole transition ( $M1$ ) of  $^{57}\text{Fe}$ , the ( $2^+ \rightarrow 0^+$ ) electric quadrupole transition ( $E2$ ) of  $^{156}\text{Gd}$ , the ( $5/2^+ \rightarrow 7/2^+$ ) magnetic dipole transition ( $M1$ ) of  $^{151}\text{Eu}$ , and the ( $1/2^+ \rightarrow 3/2^+$ ) mixed transition ( $M1/E2$ ) of  $^{197}\text{Au}$ . The third section describes in great detail the calculation of the intensity of the Mössbauer absorption lines. It introduces the density matrix of the radiation, the absorber matrix, the intensity matrix, and the texture, super-texture, and  $f$ -factor coefficients. For the nuclear transitions above the different matrices are explicitly

calculated. In Section 4 the theory is applied to thin absorbers. It may be helpful to read this section first to get an impression of the unusual formulation in comparison with the evaluation of the measurements as commonly described in the literature. Thick absorbers are treated in the last section, which requires a detailed knowledge of Section 3. Although this chapter has grown to an extensive size, it deals only with a small selection of the possible experimental situations. It describes only absorption experiments on Mössbauer nuclei which are subjected to stationary electric field gradients of different orientations.

### 1. The Quadrupole Interaction

Following, for example, Abragam and Bleaney,<sup>19</sup> the interaction  $W$  between the nuclear charge distribution  $\rho_n(\mathbf{r}_n)$  of the nucleus of interest and the charge distribution of the rest of the crystal is given by the integral [ $1/(4\pi\epsilon_0)$  is dropped]

$$W = \int_{\tau_n} \int_{\tau} \frac{\rho_n(\mathbf{r}_n) \rho(\mathbf{r})}{|\mathbf{r}_n - \mathbf{r}|} d\tau_n d\tau \quad (1.1)$$

Since the  $s$  electrons which penetrate the nucleus do not contribute to quadrupole effects, the charge density  $\rho$  does not contain the electron density of the  $s$  electrons. Then  $\rho(\mathbf{r})$  vanishes for  $r \leq r_n$  and the quotient  $1/|\mathbf{r}_n - \mathbf{r}|$  is expanded in the power series

$$\frac{1}{|\mathbf{r}_n - \mathbf{r}|} = \sum_{k=0}^{\infty} \sum_{m=-k}^k \frac{4\pi}{2k+1} \frac{r_n^k}{r^{k+1}} Y_{km}(\vartheta_n, \varphi_n) Y_{km}^*(\vartheta, \varphi) \quad (1.2)$$

Equation (1.1) is written as a sum of scalar products of tensors of rank  $k$ :

$$W = \sum_{k=0}^{\infty} \sum_{m=-k}^k (-)^m Q_{km} C_{k-m} \quad (1.3)$$

where

$$Q_{km} = \left( \frac{4\pi}{2k+1} \right)^{1/2} \int_{\tau_n} \rho_n(\mathbf{r}_n) r_n^k Y_{km}(\vartheta_n, \varphi_n) d\tau_n \quad (1.4a)$$

$$C_{km} = \left( \frac{4\pi}{2k+1} \right)^{1/2} \int_{\tau} \rho(\mathbf{r}) r^{-(k+1)} Y_{km}(\vartheta, \varphi) d\tau \quad (1.4b)$$

We are only interested in the quadrupole interaction, which is the term with  $k=2$

$$W_Q = \sum_{m=-k}^k (-)^m Q_{2m} C_{2-m} \quad (1.5)$$

To calculate the  $Q_{2m}$  of a nucleus in the state  $|IM\rangle$  which is described by the wave function  $\psi_{IM}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_A)$  of the coordinates of its  $A$  nucleons, the nuclear charge density  $\rho_n(\mathbf{r}_n)$  has to be expressed by the wave function. The charge density at  $\mathbf{r}$  is the expectation value of the operator

$$\hat{\rho}_n(\mathbf{r}_n) = \sum_{i=1}^A q_i \delta(\mathbf{R}_i - \mathbf{r}_n) \quad (1.6)$$

which is the sum of the proton and neutron point charges at  $\mathbf{R}_i$ , where  $q_i = e$  for a proton and  $q_i = 0$  for a neutron. The expectation value  $(\psi_{IM}|\hat{\rho}_n|\psi_{IM})$  inserted in equation (1.4) gives after integration over  $d\tau_n$

$$Q_{2m} = \left(\frac{4\pi}{5}\right)^{1/2} \int \psi_{IM}^* \sum_{i=1}^A q_i R_i^2 Y_{2m}(\theta_i, \phi_i) \psi_{IM} d\mathbf{R}_1 \cdots d\mathbf{R}_A \quad (1.7)$$

So  $Q_{2m}$  is written as an expectation value of the nuclear operator

$$\hat{Q}_{2m} = \left(\frac{4\pi}{5}\right)^{1/2} \sum_{i=1}^A q_i R_i^2 Y_{2m}(\theta_i, \phi_i) \quad (1.8)$$

$R_i, \theta_i, \phi_i$  are the polar coordinates of the nucleon at  $\mathbf{R}_i$ . The  $\hat{Q}_{2m}$  expressed by the Cartesian coordinates which will be used below are given by

$$\begin{aligned} \hat{Q}_{20} &= \frac{1}{2} \sum_i q_i (3Z_i^2 - R_i^2) \\ \hat{Q}_{2\pm 1} &= \pm \left(\frac{3}{2}\right)^{1/2} \sum_i q_i Z_i (X_i \pm iY_i) \\ \hat{Q}_{2\pm 2} &= \left(\frac{3}{8}\right)^{1/2} \sum_i q_i (X_i \pm iY_i)^2 \end{aligned} \quad (1.9)$$

Within the manifold of the  $2I+1$  spin states  $|IM\rangle$  of the nucleus, the matrix elements of a tensor operator is evaluated by the Wigner-Eckart theorem. In addition to a common factor, the reduced matrix element  $(I||\hat{Q}_2||I)$ , we have

$$\langle IM' | \hat{Q}_{2m} | IM'' \rangle = (-)^{I-M'} \begin{pmatrix} I & 2 & I \\ -M' & m & M'' \end{pmatrix} (I || \hat{Q}_2 || I) \quad (1.10)$$

The reduced matrix element is proportional to the quadrupole moment  $Q$  of the nucleus, which is defined by  $eQ = 2(I || \hat{Q}_{20} || I)$ , so that

$$(I || \hat{Q}_2 || I) = \frac{1}{2} eQ \begin{pmatrix} I & 2 & I \\ -I & 0 & I \end{pmatrix}^{-1} \quad (1.11)$$

Instead of handling the  $3j$  symbols of Wigner it is more convenient to use equivalent operators  $\hat{q}_{2m}$  which are constructed from the spin operators  $I_x, I_y, I_z$  acting on the magnetic quantum numbers  $M$  of the states  $|IM\rangle$ . If they transform with respect to rotations in the same way as the  $\hat{Q}_{2m}$ , their matrix elements are related by a common factor. Since the polar vector  $\mathbf{R} = (X, Y, Z)$  and the axial vector  $\mathbf{I} = (I_x, I_y, I_z)$  have the same transformation property with respect to rotations, the  $\hat{q}_{2m}$  operators are constructed in analogy to the  $\hat{Q}_{2m}$ :

$$\begin{aligned} \hat{q}_{20} &= \langle \hat{q}_2 \rangle \frac{1}{2} (3I_z^2 - I^2) \\ \hat{q}_{2\pm 1} &= \mp \langle \hat{q}_2 \rangle \left( \frac{3}{2} \right)^{1/2} [\frac{1}{2}(I_z I_{\pm} + I_{\pm} I_z)] \\ \hat{q}_{2\pm 2} &= \langle \hat{q}_2 \rangle \left( \frac{3}{8} \right)^{1/2} I_{\pm}^2 \end{aligned} \quad (1.12)$$

The  $I_z I_{\pm}$  operator ( $I_{\pm} = I_x \pm iI_y$ ) has to be symmetrized to obtain a symmetric tensor operator. The common factor  $\langle \hat{q}_2 \rangle$  is found by comparing one expectation value of one of the  $\hat{q}_{2m}$  and  $\hat{Q}_{2m}$  operators. With the choice  $|II\rangle$  and  $m=0$  one finds immediately  $\langle \hat{q}_2 \rangle = eQ[3I^2 - I(I+1)]^{-1}$ . The Hamilton operator of the quadrupole interaction acting on the spin states  $|IM\rangle$  is now given by equation (1.5) replacing the values  $Q_{2m}$  by the operators  $\hat{q}_{2m}$ .

Usually the Hamilton operator is expressed by the Cartesian components of the electric field gradient (EFG) instead of the spherical components  $C_{2m}$ . If  $V(\mathbf{r})$  is the potential produced by the charge distribution  $\rho(\mathbf{r})$ , the electric field is the negative gradient of the potential:  $-\partial V/\partial i, i = x, y, z$ . The negative gradients of the electric field components  $\partial^2 V/\partial i \partial k = V_{ik}$  are the tensor components of the electric field gradient. The relation between the tensor components  $C_{2m}$  and the  $V_{ik}$  is easily obtained by inserting a special charge distribution  $\rho(\mathbf{r}) = \sum_i e_i \delta(\mathbf{r}_i - \mathbf{r})$  in equation (1.4b) and by calculating the second derivatives of the corresponding potential  $V = \sum_i e_i |\mathbf{r}_i - \mathbf{r}|^{-1}$  at  $\mathbf{r} = 0$ . The following relations are derived:

$$\begin{aligned}
 C_{20} &= \frac{1}{2}V_{zz} \\
 C_{2\pm 1} &= \mp \frac{1}{\sqrt{6}}(V_{xz} \pm iV_{yz}) \\
 C_{2\pm 2} &= \frac{1}{2\sqrt{6}}(V_{xx} - V_{yy} \pm 2iV_{xy})
 \end{aligned} \tag{1.13}$$

The trace of the symmetric EFG tensor ( $V_{ik} = V_{ki}$ ) vanishes as a result of the Laplace equation  $\Delta V = 0$  at  $\mathbf{r} = 0$ . The tensor is diagonal in its principal axes system (PAS), which can be chosen so that the asymmetry parameter  $\eta = (V_{xx} - V_{yy})/V_{zz}$  is positive and not greater than 1. Then the tensor is specified by two independent parameters,  $V_{zz}$  and  $\eta$ :

$$(V_{ik}) = V_{zz} \begin{pmatrix} -(1 - \eta)/2 & & \\ & -(1 + \eta)/2 & \\ & & 1 \end{pmatrix} \tag{1.14}$$

The Hamilton operator of the quadrupole interaction equation (1.4) in the PAS of the EFG has now the familiar form

$$H = \frac{eQV_{zz}}{4I(2I - 1)} \left[ 3I_z^2 - I(I + 1) + \frac{\eta}{2}(I_+^2 + I_-^2) \right] \tag{1.15}$$

The information on the charge distribution  $\rho(\mathbf{r})$  is comprised in the five independent components of the EFG, which can be represented by  $V_{zz}$ ,  $\eta$ , and the three Euler angles  $\varphi$ ,  $\vartheta$ ,  $\psi$ , describing the orientation of the PAS. It is useful to consider the invariants of the tensor  $V_{ik}$  with respect to rotations. The trivial invariant  $\phi_1$  is the trace of the tensor  $V_{ik}$ ; it is  $\phi_1 = \sum_i V_{ii} = 0$ . According to equation (1.3) we can calculate a second invariant  $\phi_{II} = \sum_m (-)^m C_{2m} C_{2-m}$ , which gives in Cartesian coordinates [equation (1.13)]

$$\phi_{II} = \frac{1}{4}[V_{zz}^2 + \frac{1}{3}(V_{xx} - V_{yy})^2 + \frac{4}{3}(V_{xy}^2 + V_{xz}^2 + V_{yz}^2)] \tag{1.16}$$

$\phi_{II}$  can also be expressed by the negative average of the three symmetric  $2 \times 2$  determinants of the  $V_{ik}$  matrix:

$$\phi_{II} = -\frac{1}{3} \left\{ \begin{vmatrix} V_{xx} & V_{xy} \\ V_{yx} & V_{yy} \end{vmatrix} + \begin{vmatrix} V_{xx} & V_{xz} \\ V_{zx} & V_{zz} \end{vmatrix} + \begin{vmatrix} V_{yy} & V_{yz} \\ V_{zy} & V_{zz} \end{vmatrix} \right\} \tag{1.17}$$

In anticipation of results on the  $^{57}\text{Fe}$  ( $3/2^- \rightarrow 1/2^-$ ) transition, we will call the energy  $|eQ|\sqrt{\phi_{II}}$  the quadrupole splitting  $\Delta E_Q$ .  $\Delta E_Q$  is the well-known separation of the Mössbauer absorption lines of an  $^{57}\text{Fe}$  nucleus subjected to an EFG. In the PAS of the EFG the second invariant is taken from equation (1.14):

$$\phi_{II} = \frac{1}{4}V_{zz}^2(1 + \eta^2/3) \quad (1.18)$$

The next higher invariant is obtained by the coupling of the tensor products  $C_{2m} \cdot C_{2m'} \cdot C_{2m''}$  to a scalar. This scalar is proportional to the determinant of the  $V_{ik}$  tensor matrix. We define  $\phi_{III} = |V_{ik}|$ :

$$\begin{aligned} \phi_{III} = & V_{xx}V_{yy}V_{zz} + 2V_{xy}V_{xz}V_{yz} \\ & - V_{xx}V_{yz}^2 - V_{yy}V_{xz}^2 - V_{zz}V_{xy}^2 \end{aligned} \quad (1.19)$$

In the PAS of the EFG we have simply

$$\phi_{III} = V_{zz}^3(1 - \eta^2)/4 \quad (1.20)$$

## 2. The Line Positions of a Mössbauer Spectrum

The line positions contain only information on the invariants  $\phi_{II}$ ,  $\phi_{III}$  and none on the orientation of the EFG. To determine both invariants from the positions alone the spectrum must consist of at least three lines to measure two energy differences. Only the simple quadrupole split spectrum of the ( $3/2 \rightarrow 1/2$ ) transition exhibits two lines, the separation being  $|eQ|\sqrt{\phi_{II}}$ . Transitions with higher spin values uniquely determine both invariants and therewith  $V_{zz}$  and  $\eta$ . In Section 2.1 the Hamilton matrix is set up for  $I = 3/2, 5/2, 7/2$ , and 2. In the case of  $I = 3/2, 2$  the eigenstates and eigenvalues depending on  $\eta$  are given analytically, whereas the eigenvalues of the  $I = 5/2$  and  $I = 7/2$  spin Hamiltonian are plotted versus  $\eta$ . A plot of the line positions versus  $\eta$  of the ( $5/2^+ \rightarrow 7/2^+$ ) transition of  $^{151}\text{Eu}$  is illustrated in Section 2.2.

The reverse procedure which starts with line positions and calculates the energies of the spin states and from these  $V_{zz}$  and  $\eta$  is described by Williams and Bancroft.<sup>20</sup> For pure quadrupole interaction this procedure is trivial and therefore will not be described here.

### 2.1. The Eigenvalues of the Spin Hamiltonian

The Hamiltonian representing the interaction of a nucleus with spin  $I$  and quadrupole moment  $Q$  with an electric field gradient is written according to equation (1.15):

$$H = \frac{eQV_{zz}}{4I(2I-1)} \left[ 3I_z^2 - I(I+1) + \frac{\eta}{2} (I_+^2 + I_-^2) \right] \quad (2.1)$$

The coordinate system  $S^E$  will denote the PAS of the EFG. The Hamilton matrix  $\langle Im|H|Im' \rangle = H_{mm'}$  is constructed with the basis set  $|Im\rangle$ , the  $z$  axis of the system  $S^E$  being the quantization axis ( $I_z|Im\rangle = m|Im\rangle$ ). The secular determinant  $|H_{mm'} - E_\beta \delta_{mm'}|$  vanishes for the  $2I+1$  eigenvalues  $E_\beta$ . The eigenstates  $|Ie_\beta\rangle = \sum_m e_{\beta m} |Im\rangle$  are obtained from the linear equations

$$\sum_{m'} H_{mm'} e_{\beta m'} = E_\beta e_{\beta m} \quad (2.2)$$

The energies  $E_\beta$  will be measured in units of<sup>20</sup>  $\mu_I = eQV_{zz}/4I(2I-1)$ . Then they depend only on the asymmetry parameter  $\eta$ . In the following the eigenvalues and eigenstates of the  $I = 1/2, \dots, 7/2$  spin Hamiltonian of equation (2.1) are presented.

(i) The  $I = 1/2$  Kramers doublet remains degenerate in an electric field.

(ii) The  $I = 3/2$  Hamiltonian is given by

$$(H_{ik}) = \mu_{3/2} \begin{pmatrix} 3 & 0 & \sqrt{3}\eta & 0 \\ 0 & -3 & 0 & \sqrt{3}\eta \\ \sqrt{3}\eta & 0 & -3 & 0 \\ 0 & \sqrt{3}\eta & 0 & 3 \end{pmatrix} \equiv \mu_{3/2}(h_{ik}) \quad (2.3)$$

The eigenvalues of  $(h_{ik})$  will be denoted by  $\epsilon_i$ . The matrix decomposes into two matrices which are related to each other by a unitary transformation. The eigenvalues and eigenstates are<sup>21</sup>

$$\begin{aligned} \epsilon_+ = \epsilon_{1,2} &= 3(1 + \eta^2/3)^{1/2}, & |\tfrac{3}{2}e_1\rangle &= e_+ |\tfrac{3}{2} \tfrac{3}{2}\rangle + e_- |\tfrac{3}{2} - \tfrac{1}{2}\rangle \\ & & |\tfrac{3}{2}e_2\rangle &= e_+ |\tfrac{3}{2} - \tfrac{3}{2}\rangle + e_- |\tfrac{3}{2} \tfrac{1}{2}\rangle \\ \epsilon_- = \epsilon_{3,4} &= -\epsilon_+, & |\tfrac{3}{2}e_3\rangle &= e_- |\tfrac{3}{2} \tfrac{3}{2}\rangle - e_+ |\tfrac{3}{2} - \tfrac{1}{2}\rangle \\ & & |\tfrac{3}{2}e_4\rangle &= e_- |\tfrac{3}{2} - \tfrac{3}{2}\rangle - e_+ |\tfrac{3}{2} \tfrac{1}{2}\rangle \end{aligned} \quad (2.4)$$

where  $e_\pm = 2^{-1/2} [1 \pm (1 + \eta^2/3)^{-1/2}]^{1/2}$ . The four spin states split into two Kramers doublets. The two states of each doublet are related by the time inversion operator  $\theta$ :  $\theta|\tfrac{3}{2}e_1\rangle = |\tfrac{3}{2}e_2\rangle$  and  $\theta|\tfrac{3}{2}e_3\rangle = |\tfrac{3}{2}e_4\rangle$ . The splitting  $\Delta E_Q = 2|\mu_{3/2}\epsilon_+|$  is proportional to the square root of the second invariant  $\phi_{II}$  of the EFG tensor:



$$\Delta E_Q = |eQ|\sqrt{\phi_{11}} \quad (2.5)$$

For the axial EFG tensor ( $\eta = 0 \Rightarrow e_- = 0$ ) the Kramers conjugate states  $|3/2 \pm m\rangle$  are eigenstates.

(iii) The  $I = 2$  Hamiltonian. The reduced matrix ( $h_{ik}$ ) is given by

$$(h_{ik}) = \begin{pmatrix} 6 & 0 & \sqrt{6}\eta & 0 & 0 \\ 0 & -3 & 0 & 3\eta & 0 \\ \sqrt{6}\eta & 0 & -6 & 0 & \sqrt{6}\eta \\ 0 & 3\eta & 0 & -3 & 0 \\ 0 & 0 & \sqrt{6}\eta & 0 & 6 \end{pmatrix} \quad (2.6)$$

The matrix decomposes into a two- and three-dimensional matrix. The solution for the  $2 \times 2$  matrix is as follows (the quantum number  $I$  of the states is dropped):

$$\begin{aligned} \epsilon_2 &= -3(1 + \eta), & |e_2\rangle &= 2^{-1/2} (|1\rangle - |-1\rangle) \\ \epsilon_3 &= -3(1 - \eta), & |e_3\rangle &= 2^{-1/2} (|1\rangle + |-1\rangle) \end{aligned} \quad (2.7)$$

The similarity transformation

$$U \begin{pmatrix} 6 & \sqrt{6}\eta & 0 \\ \sqrt{6}\eta & -6 & \sqrt{6}\eta \\ 0 & \sqrt{6}\eta & 6 \end{pmatrix} U^+ = \begin{pmatrix} 6 & 0 & 0 \\ 0 & -6 & 2\sqrt{3}\eta \\ 0 & 2\sqrt{3}\eta & 6 \end{pmatrix} \quad (2.8)$$

with

$$U = \begin{pmatrix} 1/\sqrt{2} & 0 & -1/\sqrt{2} \\ 0 & 1 & 0 \\ 1/\sqrt{2} & 0 & 1/\sqrt{2} \end{pmatrix} \quad (2.9)$$

further decomposes the  $3 \times 3$  matrix. The two-dimensional matrix is proportional to one of the submatrices of the  $I = 3/2$  problem. So we obtain

$$\begin{aligned} \epsilon_1 &= -6(1 + \eta^2/3)^{1/2}, & |e_1\rangle &= e_- 2^{-1/2} (|2\rangle + |-2\rangle) - e_+ |0\rangle \\ \epsilon_4 &= 6, & |e_4\rangle &= 2^{-1/2} (|2\rangle - |-2\rangle) \\ \epsilon_5 &= -\epsilon_1, & |e_5\rangle &= e_+ 2^{-1/2} (|2\rangle + |-2\rangle) + e_- |0\rangle \end{aligned} \quad (2.10)$$

The coefficients  $e_{\pm}$  are the same as defined above. An axial EFG ( $\eta = 0$ ) splits the fivefold degenerate spin states into three levels, two doublets and one singlet.

(iv) The  $I = 5/2$  Hamiltonian. The six-dimensional Hamilton matrix decomposes into two  $3 \times 3$  matrices, related by a unitary transformation. One of them is written as

$$(h_{ik}) = \begin{pmatrix} 10 & 2\sqrt{5}\eta & 0 \\ 2\sqrt{5}\eta & -8 & 3\sqrt{2}\eta \\ 0 & 3\sqrt{2}\eta & -2 \end{pmatrix} \quad (2.11)$$

The eigenvalues are the roots of the secular polynomial

$$\epsilon^3 - 28(3 + \eta^2)\epsilon - 160(1 - \eta^2) = 0 \quad (2.12)$$

The degenerate eigenstates (the index of the state is dropped) are

$$|e\rangle = e_{5/2}|\frac{5}{2}\rangle + e_{1/2}|\frac{1}{2}\rangle + e_{-3/2}|\frac{3}{2}\rangle \quad (2.13)$$

and the time-inverted states

$$\theta|e\rangle = e_{5/2}|\frac{5}{2}\rangle + e_{1/2}|\frac{1}{2}\rangle + e_{-3/2}|\frac{3}{2}\rangle \quad (2.14)$$

Use has been made of  $\theta e_m|Im\rangle = (-)^{I-m}e_m^*|I-m\rangle$  and of  $e_m^* = e_m$ . In Figure 1 the eigenvalues in units of  $\mu_{5/2}$  of the three Kramers doublets are plotted versus  $\eta$ . An analytical solution has been published by S. Kareem *et al.*<sup>22</sup>

(v) The  $I = 7/2$  Hamiltonian. The eight-dimensional Hamilton matrix decomposes into two similar  $4 \times 4$  matrices, one of them being

$$(h_{ik}) = \begin{pmatrix} 21 & \sqrt{21}\eta & 0 & 0 \\ \sqrt{21}\eta & -9 & 2\sqrt{15}\eta & 0 \\ 0 & 2\sqrt{15}\eta & -15 & 3\sqrt{5}\eta \\ 0 & 0 & 3\sqrt{5}\eta & 3 \end{pmatrix} \quad (2.15)$$

with the secular polynomial

$$\epsilon^4 - 126(3 + \eta^2)\epsilon^2 - 1728(1 - \eta^2)\epsilon + 945(3 + \eta^2)^2 = 0 \quad (2.16)$$

The degenerate eigenstates for each eigenvalue are

$$|e\rangle = e_{7/2}|\frac{7}{2}\rangle + e_{3/2}|\frac{3}{2}\rangle + e_{-1/2}|\frac{1}{2}\rangle + e_{-5/2}|\frac{5}{2}\rangle \quad (2.17)$$

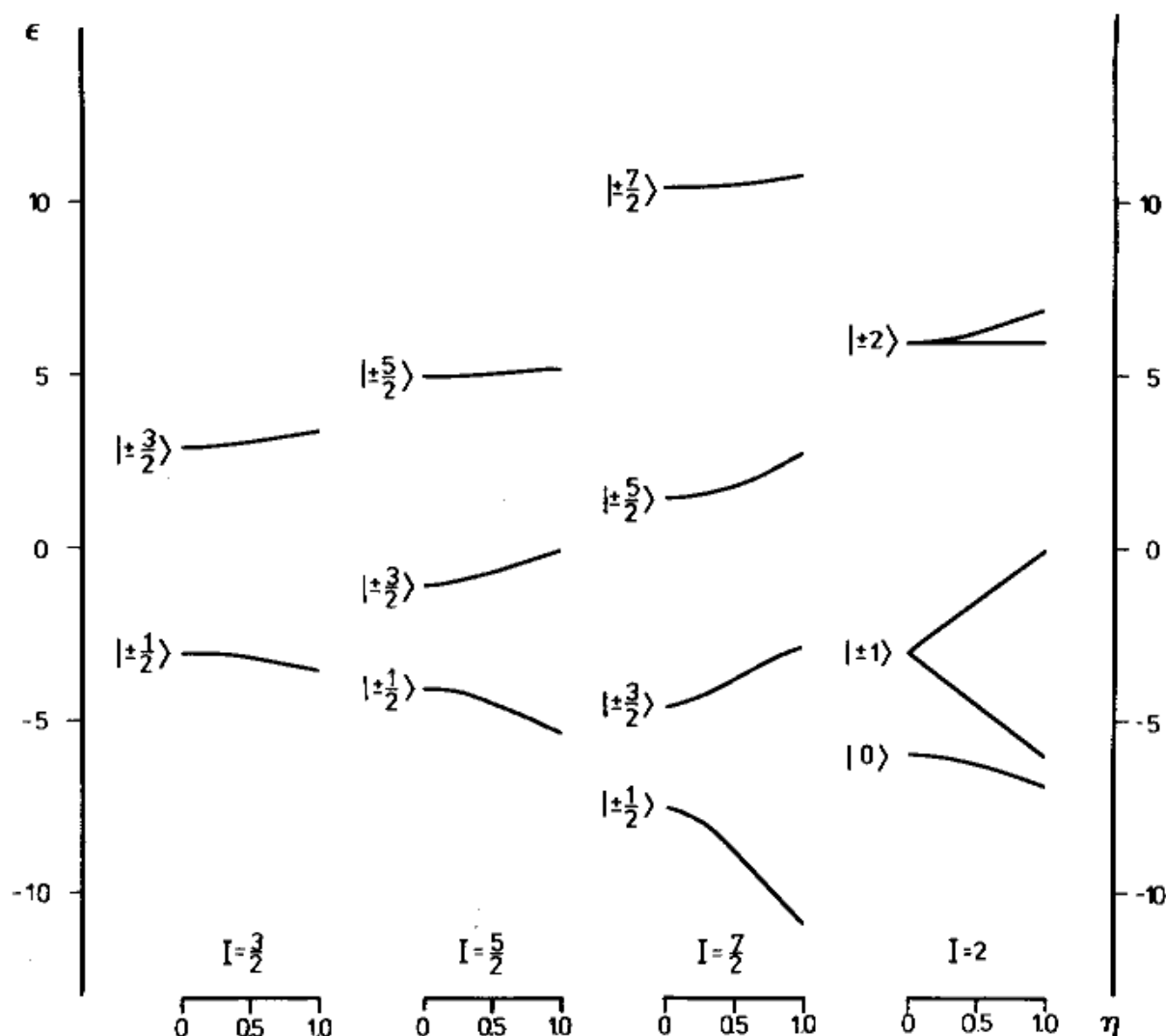


FIGURE 1. The energy splitting of the various spin states is plotted versus the asymmetry parameter  $\eta$  of the electric field gradient. The energies are given in units of  $\mu_f = eQV_{zz}/4I(2I-1)$  for the  $I = 3/2, 2$ , and  $2\mu_f$  for  $I = 5/2, 7/2$ .

and  $\theta|e\rangle$ . The plot of the eigenvalues of the four Kramers doublets versus  $\eta$  is shown in Figure 1. Analytical expressions have also been calculated.<sup>22</sup>

Comparing the four plots in Figure 1 two facts are obvious:

( $\alpha$ ) the gradients  $\partial\epsilon_i/\partial\eta$  vanish at  $\eta = 0$  for half-integral spins. It is therefore difficult to observe small  $\eta$  values. For the integral spin  $I = 2$  the splitting of the  $|\pm 1\rangle$  level linearly increases with increasing  $\eta$  and therefore becomes sensitive to small deviations from  $\eta = 0$ .

( $\beta$ ) At  $\eta = 1$  the energy level schemes are symmetric to the center ( $\epsilon = 0$ ).

## 2.2. The Information Obtained from the Line Positions

The energy differences  $\Delta_{ik} = E_i(I_e) - E_k(I_g)$  of the energies  $E_i$  of the excited ( $I_e$ ) and the ground states ( $I_g$ ) are proportional to the line positions

(in mm/s) measured with respect to the isomer shift of the spectrum. If one of the levels are not split ( $I = 1/2$ ) the line positions are just given by the plots of  $\epsilon_k(\eta)$  of Figure 1 apart from a scaling factor. Examples are the ( $I_e = 3/2 \rightarrow I_g = 1/2$ ) transition of  $^{57}\text{Fe}$ , the ( $I_e = 1/2 \rightarrow I_g = 5/2$ ) transition of  $^{67}\text{Zn}$ , and the ( $I_e = 2 \rightarrow I_g = 0$ ) transitions. In these cases the scaling factors are  $\mu_I \cdot c/E_0$ , where  $c$  is the velocity of light and  $E_0$  is the transition energy. As an example of a more complex scheme the ( $I_e = 5/2 \rightarrow I_g = 7/2$ ) transition of  $^{151}\text{Eu}$  is considered. The scaling factors are different in both states; their ratio is determined by the ratios of the quadrupole moments  $Q_e/Q_g = 1.34$ .<sup>23</sup> The energy difference may be written

$$\Delta_{ik} = \mu_{I_e} \cdot \epsilon_i(I_e) - \mu_{I_g} \cdot \epsilon_k(I_g) = \mu_{I_g} \left[ \frac{Q_e}{Q_g} \epsilon_i(I_e) - \epsilon_k(I_g) \right] \quad (2.18)$$

so that the scaling factor of the spectrum  $\delta_{ik} = \mu_{I_e}/\mu_{I_g} \epsilon_i(I_e) - \epsilon_k(I_g)$  is given by  $\mu_{I_g} \cdot c/E_0$ . Figure 2 shows the line positions  $\delta_{ik}(\eta)$ . All energy differences are shown. The intensities of several lines vanish for special directions of the observation or generally by the rules of the conservation of angular momentum. In the stick diagram on the top of the Figure 2 the

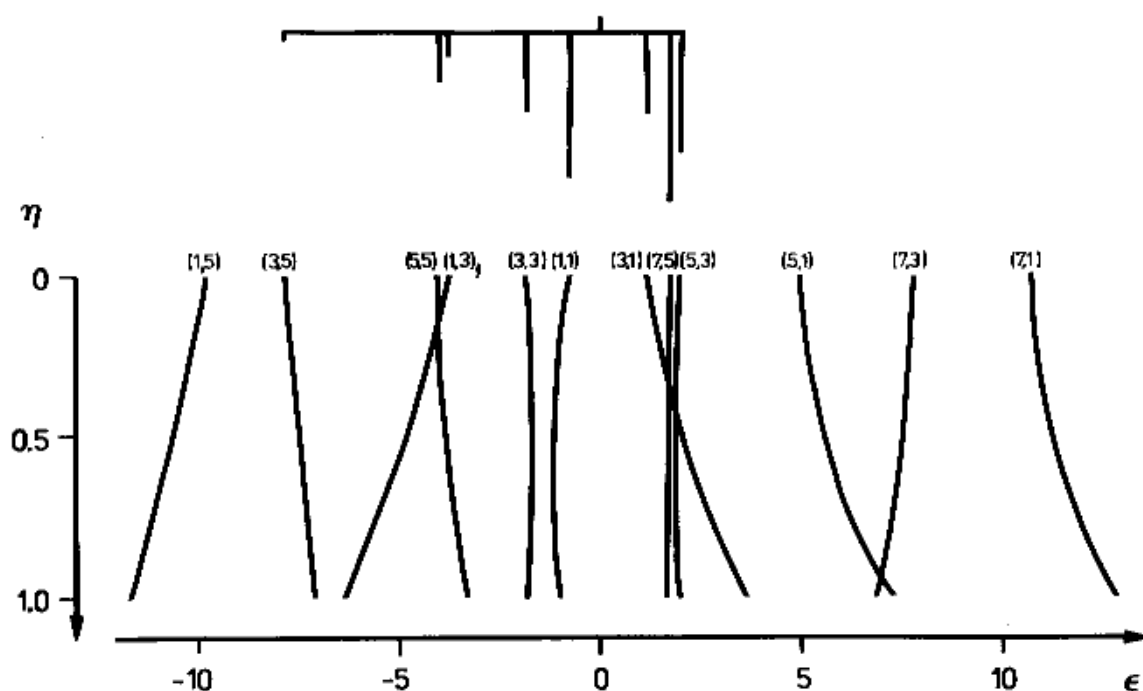


FIGURE 2. The dependence of the line positions  $\delta_{ik}$  on the asymmetry parameter  $\eta$  is shown for an ( $I_e = 7/2 \rightarrow I_g = 5/2$ ) transition. The ratio  $\mu_{I_e}/\mu_{I_g} = 0.638$  corresponds to the ratio of the quadrupole moments  $Q_e/Q_g = 1.34$  of the 21.6-keV transition of  $^{151}\text{Eu}$ . The velocity is given in units of  $\mu_{I_g} c/E_0$ . The symbols  $(n, m)$  stand for the transition  $(\pm n/2 \rightarrow \pm m/2)$ , where the  $|\pm m/2\rangle$  are the eigenstates of an axial EFG. On the top of the figure is the stick diagram of the spectrum at  $\eta = 0$  with the intensities of a thin powder absorber in the case of a M1 transition.

intensities of a powder absorber are shown for the case of a  $M1$  transition as will be calculated in Section 3.2.2. The scaling factor determines the principal component  $V_{zz}$  of the EFG, its absolute value and sign. The  $\eta$  value is found by adjusting the scaling factor to such a value that all position match the  $\delta_{ik}$  of Figure 2 at one horizontal cut of the diagram.

### 3. The Intensities of the Mössbauer Absorption Spectra

The general formalism for the calculation of the intensities of a Mössbauer spectrum are developed as far as possible without specifying the eigenstates of the nuclei. This procedure is prescribed by the concept of the intensity matrix and of the texture components of the absorber. In the first subsection the absorption of a polarized  $\gamma$  ray by an optically active absorber is outlined by use of the intensities matrices, which are explicitly calculated in Section 3.2 for the Mössbauer transitions under consideration.

In general the absorber contains a distribution of the PAS of the EFG tensors. This distribution is described by the probability  $T(\alpha, \beta, \gamma)d\Omega$ , where  $T(\alpha, \beta, \gamma)$  is called the texture function which characterizes the textured powder absorbers as well as single crystals with different equivalent sites. The texture function is expanded in a series of the  $(2L+1)$ -dimensional rotation matrices  $D_{m'm}^L(\beta)$  [the Euler angles are denoted by  $\beta = (\alpha, \beta, \gamma)$ ]:

$$T(\beta) = \sum_{L,m',m} t_{m'm}^L D_{m'm}^L(\beta) \quad (3.1)$$

The coefficients  $t_{m'm}^L$  are the so-called texture components. The calculation of the intensities of the Mössbauer spectra by use of these texture components of the absorbers is the subject of Section 3.3. A similar expansion of the Debye-Waller factor  $f$  is given by<sup>15</sup>

$$f(\beta) = \sum_{L,m} f_m^L D_{0m}^L(\beta) \quad (3.2)$$

where  $\vartheta = \beta$  and  $\varphi = \pi - \gamma$  are the polar angles of the  $\gamma$ -ray direction  $\mathbf{k}$  with respect to the PAS of the EFG tensor. The dependence of the intensities on the coefficients  $f_m^L$  of random powders (Goldanskii-Karyagin effect) and of textured absorbers (introduction of super-texture components) is the content of Section 3.4.

#### 3.1. The Matrix Formulation

The propagation of electromagnetic radiation in matter is an important subject in spectroscopy. In the visible region the different phenomena,

such as Faraday rotation, circular birefringence, dechroism, are well known. In the  $\gamma$ -ray region these effects are usually unimportant as a result of the small electronic absorption. The situation changes, however, for resonantly absorbing Mössbauer nuclei. For example, Faraday rotation of polarized  $\gamma$ -rays has been observed by the Mössbauer effect with  $^{57}\text{Fe}$  nuclei.<sup>24,25</sup> Further examples can be found in the review article of Gonser and Fischer.<sup>26</sup> A general treatment of the resonance absorption of polarized  $\gamma$ -rays and of the polarization of the propagating wave has been given in terms of a complex  $2 \times 2$  matrix of the index of refraction.<sup>2</sup> The following three subsections deal with the density matrix of the radiation, the index of refraction, the intensity matrix, and the calculation of a Mössbauer spectrum. The theory is at this stage quite general and not restricted to pure quadrupole interaction.

### 3.1.1. The Absorption of Polarized Radiation

According to classical optics the electric field of an electromagnetic plane wave traveling in the  $z$  direction through a medium with the index of refraction  $n$  is given by

$$\mathbf{E} = \exp(inkz)\mathbf{E}_0 \quad (3.3)$$

The time-dependent phase factor  $\exp(-i\omega t)$  is dropped.  $\mathbf{k} = k\mathbf{e}_z$  is the wave vector and  $\mathbf{E}_0$  the electric field at  $z = 0$ . In vacuum the index of refraction is  $n = 1$  and  $\exp(ikz)$  is the phase factor at the position  $z$ . In an absorbing medium  $n$  becomes a complex  $2 \times 2$  matrix which generally cannot be diagonalized by an unitary transformation. To begin with the case of a diagonal  $n$  is considered.  $n_x$  and  $n_y$  are the indices of refraction with respect to the optical axes  $\mathbf{e}_x$ ,  $\mathbf{e}_y$  of the medium. The components  $E_x$  and  $E_y$  independently travel through the medium. The equation (3.3) decomposes into two equations

$$\begin{aligned} E_x &= e^{in_x kz} E_{0x} \\ E_y &= e^{in_y kz} E_{0y} \end{aligned} \quad (3.4)$$

as a result of the matrix equation

$$\exp\begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix} = \begin{pmatrix} \exp(a) & 0 \\ 0 & \exp(b) \end{pmatrix} \quad (3.5)$$

$n_x$  and  $n_y$  are complex numbers, the imaginary part is related to the absorption and the real part to the dispersion phenomenon. If the vector  $\mathbf{E}_0$

is an eigenvector of  $n$ , then the direction of  $\mathbf{E}$  is conserved. This is the case for  $\mathbf{E}$  parallel to the optical PAS. An arbitrary  $\mathbf{E}$  vector is rotated in the  $e_x, e_y$  plane with increasing  $z$ .

We are now interested in the intensity  $\propto |\mathbf{E}|^2$  at  $z=d$ , the thickness of the absorber, compared to the intensity at  $z=0$  of the incident wave. The ratio  $I/I_0 = |\mathbf{E}|^2/|\mathbf{E}_0|^2$  can be written as ( $\mathbf{E}$  is a column vector)

$$I/I_0 = \mathbf{E}^+ \mathbf{E} / |\mathbf{E}_0|^2 \quad (3.6)$$

Inserting the vector of equation (3.3) gives step by step

$$\begin{aligned} \mathbf{E}^+ \mathbf{E} &= (e^{inkz} \mathbf{E}_0)^+ (e^{inkz} \mathbf{E}_0) \\ &= \mathbf{E}_0^+ e^{-in^+ kz} e^{inkz} \mathbf{E}_0 \\ &= \sum_{\alpha, \beta, s} E_{0\beta}^* (e^{-in^+ kz})_{\beta s} (e^{inkz})_{s\alpha} E_{0\alpha} \end{aligned} \quad (3.7)$$

The product  $E_{0\alpha} E_{0\beta}^* / |\mathbf{E}_0|^2 = \rho_{0,\alpha\beta}$  is called the density matrix or coherence matrix of the wave. With this matrix we obtain for the intensity ratio

$$I/I_0 = \text{Tr}(e^{inkz} \rho_0 e^{-in^+ kz}) \quad (3.8)$$

This is the basic equation for the calculation of the absorption of the  $\gamma$  radiation. The density matrix of the radiation at  $z=d$  is obtained calculating  $E_\beta^* E_\alpha$  instead of  $\mathbf{E}^+ \mathbf{E}$ :

$$I(d)\rho = I_0 e^{inkd} \rho_0 e^{-in^+ kd} \quad (3.9)$$

The complicated expressions of equation (3.8) and (3.9), where non-Hermitian matrices appear as exponents in the exponential factors, have been calculated by use of the properties of the Pauli matrices.<sup>2</sup> These formulas will be given at the end of this subsection after some considerations about the density matrix  $\rho$ .

A coherent superposition  $\Sigma_v \mathbf{E}_v = E_x \mathbf{e}_x + E_y \mathbf{e}_y$  of arbitrary waves  $\mathbf{E}_v$  (same frequency) leads to the density matrix

$$\rho = \begin{pmatrix} \cos^2 \varphi & \frac{1}{2} \sin 2\varphi e^{i\alpha} \\ \frac{1}{2} \sin 2\varphi e^{-i\alpha} & \sin^2 \varphi \end{pmatrix} \quad (3.10)$$

where  $\cos \varphi = |E_x| / (|E_x|^2 + |E_y|^2)^{1/2}$  and  $\alpha = \alpha_x - \alpha_y$  is the difference of the phases of  $E_k = |E_k| e^{i\alpha_k}$ ,  $k = x, y$ . The matrix  $\rho$  has the properties

$$\rho^2 = \rho \quad \text{and} \quad \text{Tr}(\rho) = 1 \quad (3.11)$$

Completely unpolarized light is an incoherent superposition of waves with randomly distributed angles  $\alpha, \varphi$ . Each wave is treated according to equation (3.8), so that the measured intensity is the average over all waves resulting in the average of  $\rho_0$ .<sup>27</sup> Therefore, the density matrix  $\rho_u$  for unpolarized light becomes ( $\overline{\sin^2 \varphi} = 1/2, \overline{\sin 2\varphi} = 0$ )

$$\rho_u = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix} \quad (3.12)$$

The square of  $\rho_u$  is no longer  $\rho_u$ . The property  $\rho^2 = \rho$  proves the complete polarization of the wave. The density matrix can be thought of as an incoherent superposition of pure  $\mathbf{e}_x$  and  $\mathbf{e}_y$  polarized waves or any other orthogonal basis states. The Hermitian density matrix  $\rho$  has two real eigenvalues. The absolute value  $\xi$  of the difference of the eigenvalues is the polarization degree of the radiation. For unpolarized radiation  $\xi(\rho_u) = 0$ , and generally

$$\xi = [1 - 4 \text{Det}(\rho)]^{1/2} \quad (3.13)$$

The electric vector  $\mathbf{E}$  usually is not given with respect to the  $(\mathbf{e}_x, \mathbf{e}_y)$  basis of linear polarization but with respect to the basis  $(\mathbf{u}_1, \mathbf{u}_{-1})$  of left and right polarization, respectively,<sup>28</sup>

$$\mathbf{u}_{\pm 1} = 2^{-1/2}(\mathbf{e}_x \pm i\mathbf{e}_y), \quad \mathbf{u}_i^* \mathbf{u}_k = \delta_{ik} \quad (3.14)$$

With the vector components  $E_p = \mathbf{E} \mathbf{u}_p = 2^{-1/2}(E_x + ipE_y)$  the electric vector is written  $\mathbf{E} = E_{-1}\mathbf{u}_{-1} + E_1\mathbf{u}_1$ . The density matrix  $\rho$  can now be given with respect to the  $\mathbf{u}_p$  basis. The right  $\rho_r$  and left  $\rho_l$  circularly polarized waves are represented by the matrices

$$\rho_r = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{and} \quad \rho_l = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (3.15)$$

The matrices of linear polarized waves  $\rho_x, \rho_y$  are obtained for vanishing  $E_y$  and  $E_x$ , respectively:

$$\rho_x = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad \rho_y = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 0 \end{pmatrix} \quad (3.16a)$$

An arbitrary linear polarized wave in the direction  $\mathbf{e}_\varphi = \cos \varphi \mathbf{e}_x + \sin \varphi \mathbf{e}_y$  gives



$$\rho_{\varphi} = \frac{1}{2} \begin{pmatrix} 1 & e^{2i\varphi} \\ e^{-2i\varphi} & 1 \end{pmatrix} \quad (3.16b)$$

At last the Poincaré representation of the polarization is introduced (see U. Fano<sup>27</sup>). Let  $1_2$  be the  $2 \times 2$  unit matrix and  $\sigma_i$  the three Pauli matrices

$$\sigma_{\xi} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_{\eta} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_{\zeta} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (3.17)$$

then the density matrix is decomposed into

$$\rho = \frac{1}{2}(1_2 + \mathbf{P} \cdot \boldsymbol{\sigma}) \quad (3.18)$$

so that

$$P_{\mu} = \text{Tr}(\rho \sigma_{\mu})$$

The three real numbers  $P_{\xi}$ ,  $P_{\eta}$ ,  $P_{\zeta}$  are considered as a vector  $\mathbf{P}$  in the  $(\xi, \eta, \zeta)$  space. According to equations (3.16) and (3.17)  $\mathbf{P} = (\pm 1, 0, 0)$  represents  $x, y$  polarization and  $\mathbf{P} = (0, 0, \pm 1)$  left and right polarization. The polarization degree  $\xi$  becomes  $\xi = |\mathbf{P}|$ .

It will also be useful to express the density matrix with respect to the  $(\mathbf{e}_x, \mathbf{e}_y)$  basis by the matrix elements obtained in the  $\mathbf{u}_p$  basis. By writing the electric vector as  $\mathbf{E} = (1/\sqrt{2})(E_1 + E_{-1})\mathbf{e}_x - (i/\sqrt{2})(E_1 - E_{-1})\mathbf{e}_y$  we obtain

$$\begin{aligned} \rho_{xx} &= \frac{1}{2}(\rho_{11} + \rho_{-1-1}) + \frac{1}{2}(\rho_{1-1} + \rho_{-11}) \\ \rho_{yy} &= \frac{1}{2}(\rho_{11} + \rho_{-1-1}) - \frac{1}{2}(\rho_{1-1} + \rho_{-11}) \\ \rho_{xy} &= \frac{i}{2}(\rho_{11} - \rho_{-1-1}) - \frac{i}{2}(\rho_{1-1} - \rho_{-11}) \\ \rho_{yx} &= -\frac{i}{2}(\rho_{11} - \rho_{-1-1}) - \frac{i}{2}(\rho_{1-1} - \rho_{-11}) \end{aligned} \quad (3.19)$$

With respect to this basis the density matrices for a linearly polarized wave [equation (3.16b)] becomes

$$\rho_\varphi = \frac{1}{2} \begin{pmatrix} 1 + \cos(2\varphi) & \sin(2\varphi) \\ \sin(2\varphi) & 1 - \cos(2\varphi) \end{pmatrix} \quad (3.20)$$

and the corresponding Poincaré vector  $\mathbf{P} = (\sin(2\varphi), 0, \cos(2\varphi))$ .

After this preparation the intensity of the transmitted wave and its density matrix can be calculated. Following Blume and Kistner<sup>2</sup> the index of refraction is decomposed to

$$nkz = aI_2 + \mathbf{b} \cdot \boldsymbol{\sigma} \quad (3.21)$$

Since  $n$  is not necessarily Hermitian,  $a$  is a complex number and  $\mathbf{b}$  a complex vector. The intensity is a function of  $a, \mathbf{b}$ , and the Poincaré vector  $\mathbf{P}_0$  of the incident wave:

$$\begin{aligned} I(d)/I_0 = & \exp[i(a - a^*)] \cdot [\cos b^* \cos b + (\hat{\mathbf{b}}^* \cdot \hat{\mathbf{b}}) \sin b^* \sin b \\ & + i\mathbf{P}_0(\hat{\mathbf{b}} \cdot \sin b \cos b^* - \hat{\mathbf{b}}^* \sin b^* \cos b \\ & + (\hat{\mathbf{b}}^* \times \hat{\mathbf{b}}) \sin b^* \sin b)] \end{aligned} \quad (3.22a)$$

The Poincaré vector of the transmitted wave is given by

$$\begin{aligned} \mathbf{P}I(d)/I_0 = & \exp[i(a - a^*)] \cdot [i(\hat{\mathbf{b}} \sin b \cos b^* \\ & - \hat{\mathbf{b}}^* \sin b^* \cos b - (\hat{\mathbf{b}}^* \times \hat{\mathbf{b}}) \sin b^* \sin b) \\ & + \mathbf{P}_0 (\cos b^* \cos b - (\hat{\mathbf{b}}^* \cdot \hat{\mathbf{b}}) \sin b^* \sin b) \\ & + \mathbf{P}_0 \times (\hat{\mathbf{b}} \sin b \cos b^* + \hat{\mathbf{b}}^* \sin b^* \cos b) + \hat{\mathbf{b}}(\mathbf{P}_0 \cdot \hat{\mathbf{b}}^*) \\ & + \hat{\mathbf{b}}^*(\mathbf{P}_0 \cdot \hat{\mathbf{b}})] \end{aligned} \quad (3.22b)$$

$b$  is the complex number  $b = (b_\xi^2 + b_\eta^2 + b_\zeta^2)^{1/2}$ , and  $\hat{\mathbf{b}}$  the reduced vector  $\hat{\mathbf{b}} = \mathbf{b}/b$ .

Practically three cases are of interest, these are

- i. The transmitted intensity of an unpolarized beam ( $\mathbf{P}_0 = 0$ ), the most important case;
- ii. The transmitted intensity of a polarized beam, application of the complete equation (3.22a);
- iii. The polarization of a transmitted beam, which is originally unpolarized [ $\mathbf{P}_0 = 0$  in equation (3.22b)]; the absorber is used as a filter to obtain a polarized beam for an experiment of type (ii).

There is an important simplification of equation (3.22a) if the matrices  $n$  and  $n^+$  commute with each other:  $n \cdot n^+ = n^+ \cdot n$ . Then the product of the two exponential functions simplifies to

$$\exp(-in^+kd) \cdot \exp(inkd) = \exp[-ikd(n^+ - n)]$$

and the trace of equation (3.8) can be written

$$I(d, E) = I_0 \text{Tr}\{\rho_0 \exp[-ikd(n^+ - n)]\} \quad (3.23)$$

The Hermitian matrix  $\nu = -ikd(n^+ - n)$  is diagonalized by a unitary transformation  $U$ . If  $\nu_{ii}$  are the diagonal elements of  $U\nu U^+$  and  $\rho'_0 = U\rho_0 U^+$  is the transformed density matrix the trace can be calculated [using equation (3.5)]:

$$I(d, E) = I_0 \sum_i \rho'_{0,ii} \exp(-\nu_{ii}) \quad (3.24)$$

This special situation leading to equation (3.24) is described in the beginning of this section. The intensity calculated with the electric fields of equation (3.4) is identical with the result of equation (3.24). In a similar procedure equation (3.22b) can be simplified if  $nn^+ = n^+n$ . The case (iii) of an unpolarized incident beam is then described by the equation

$$I(d, E)\rho/I_0 = \frac{1}{2}U^+ \begin{pmatrix} \exp(-\nu_{11}) & 0 \\ 0 & \exp(-\nu_{-1-1}) \end{pmatrix} U \quad (3.25)$$

where the meaning of  $U$  is the same as above. The condition  $nn^+ = n^+n$  is realized in many practical Mössbauer experiments at least to a good approximation.

### 3.1.2. The Index of Refraction

The index of refraction of a weakly absorbing medium ( $n \sim 1$ ) containing randomly distributed scatterers is generally given by<sup>29</sup>

$$n_{pq} = \delta_{pq} + \frac{2\pi}{k^2} N F_{pq} \quad (3.26)$$

$N$  is the number of scatterers per unit volume,  $k = 2\pi/\lambda$  is the length of the wave vector  $\mathbf{k}$ , and  $F_{pq}$  is the coherent forward scattering amplitude of one scatterer. If only Mössbauer nuclei are taken into account as scatterers (the photoelectric absorption is considered at the end of this section)  $F_{pq}^\alpha$  is determined by the transition amplitude  $(a_p^{\alpha\beta})^*$  from one ground state  $|I_g g_\alpha\rangle = \sum_{m_g} g_{\alpha m_g} |I_g m_g\rangle$  to the excited states  $|I_e e_\beta\rangle = \sum_{m_e} e_{\beta m_e} |I_e m_e\rangle$  absorbing a photon of polarization  $\mathbf{u}_p$  and by the amplitude  $a_q^{\alpha\beta}$  emitting a photon of polarization  $\mathbf{u}_q$ <sup>30</sup>:

$$F_{pq}^{\alpha} = \left( \frac{kV}{2\pi\hbar c} \right) f(\mathbf{k}) \sum_{\beta} \frac{(a_p^{\alpha\beta})^* (a_q^{\alpha\beta})}{E - (E_{\beta} - E_{\alpha}) + i\Gamma/2} \quad (3.27)$$

$\beta$  runs over all excited states. The energies of the resonance denominator  $E$ ,  $E_{\alpha}$ , and  $E_{\beta}$  are those of the photon, the ground state, and the excited state, respectively.  $\Gamma$  is the width of the excited states. The prefactors are a normalization constant containing the normalized volume  $V$  of the electromagnetic field and the Debye-Waller factor  $f(\mathbf{k})$ .  $F_{pq}^{\alpha}$  has to be averaged over all ground states. At sufficiently high temperatures ( $\geq 1$  K) the ground states are equally populated, so that  $F_{pq}$  is given by

$$F_{pq} = \frac{1}{2I_g + 1} \sum_{\alpha} F_{pq}^{\alpha} \quad (3.28)$$

We consider the general case of a mixed magnetic dipole ( $M1$ ) and electric quadrupole ( $E2$ ) transition [the ( $E1/M2$ ) transition is of no importance]. The amplitudes  $a_p^{\alpha\beta}$  are given by<sup>2,28</sup>

$$a_p^{\alpha\beta}(\vartheta) = 2\pi i(\hbar c/kV)^{1/2} \sum_M M_1 V_{1M}^{\alpha\beta} D_{Mp}^1(\vartheta) - pE_2 V_{2M}^{\alpha\beta} D_{Mp}^2(\vartheta) \quad (3.29a)$$

where the tensor  $V_{LM}^{\alpha\beta}$  has been introduced<sup>11</sup>:

$$V_{LM}^{\alpha\beta} = \left( \frac{2L+1}{2I_e+1} \right)^{1/2} \sum_{m_e, m_g} e_{\beta m_e}^* g_{\alpha m_g} C(I_g L I_e, m_g M m_e) \quad (3.29b)$$

The Euler angles  $\vartheta = (\varphi, \vartheta, \psi)$  define the coordinate system  $S^{\gamma}$  with respect to the system  $S^E$  which the nuclear states are referred to. The  $z$  axis ( $\mathbf{e}_z^{\gamma}$ ) of  $S^{\gamma}$  is fixed by the Mössbauer source and the detector. The polar angles of  $\mathbf{e}_z^{\gamma}$  with respect to  $S^E$  are  $(\varphi, \vartheta)$ . The angle  $\psi$  is determined by the choice of the  $x$  axis of  $S^{\gamma}$  in the laboratory.  $D_{Mp}^L(\vartheta)$  are the  $(2L+1)$ -dimensional unitary rotation matrices. The real numbers  $M_1$  and  $E_2$  are the reduced matrix elements of the magnetic dipole and electric quadrupole transition, respectively.  $C(I_g L I_e, m_g M m_e)$  is the Clebsch-Gordan coefficient. Defining the  $2 \times 2$  absorber matrix

$$r_{pq} = (a_p^{\alpha\beta})^* a_q^{\alpha\beta} / (M_1^2 + E_2^2) \cdot (Vk/\hbar c) \quad (3.30)$$

the index of refraction is written as<sup>3</sup>

$$n_{pq} = \delta_{pq} - \frac{1}{k} \sigma_0 f(\mathbf{k}) N \cdot \sum_{\alpha\beta} \frac{1}{2} r_{pq}^{\alpha\beta} \frac{\Gamma/2}{E - (E_{\beta} - E_{\alpha}) + i\Gamma/2} \quad (3.31)$$