Polarization-Dependent Vibrational Shifts on Dielectric Substrates

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Combined Matrix formalism for the calculation of reflectance and transmittance of layered anisotropic media

The following combined matrix formalism has been introduced in [1].

The dielectric tensor of a medium is usually specified with regard to an intrinsic coordinate system *x*,*y*,*z* of a sample. To find the values of $\boldsymbol{\varepsilon}_{x,y,z}$ in a reference frame *X*,*Y*,*Z* it is necessary to employ an orthogonal transformation according to

$$\varepsilon_{X,Y,Z} = \mathbf{A}(\Omega)\cdot\boldsymbol{\varepsilon}_{x,y,z}\cdot\mathbf{A}(\Omega)^{-1}, \qquad \text{* MERGEFORMAT (1)}$$

where $\mathbf{A}(\Omega)$ is a rotation matrix. A convenient way of expressing $\mathbf{A}(\Omega)$ is e.g. to specify it by one of the 24 possible Euler angle orientation representations.[2] Further possibilities are symmetric Euler angle representations and Quarternions.[2]

In the following we assume a layered system with plane parallel interfaces normal to the *Z*-direction of a references frame and a plane wave with wave-vector $\mathbf{k}_i$ given by $\mathbf{k}_i = k_0\left(0, k_Y, k_Z\right)^T$ incident on this system (light wave incident in the *Y*-*Z* plane with an angle of incidence α). Employing first-order Maxwell-equations the dependence of the field-vector $\boldsymbol{\Psi} = \left(E_X, \quad H_Y, \quad E_Y, \quad -H_X\right)^T$ in *Z*-direction can be written as

$$\frac{\partial}{\partial Z}\boldsymbol{\psi} = ik_0\boldsymbol{\Delta}\boldsymbol{\psi}, \qquad \text{* MERGEFORMAT (2)}$$

where $\boldsymbol{\Delta}$ represents a 4×4 matrix according to

$$\boldsymbol{\Delta} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -\sin^2\alpha + \varepsilon_{XX} - \frac{\varepsilon_{XZ}^2}{\varepsilon_{ZZ}} & 0 & \varepsilon_{XY} - \frac{\varepsilon_{XZ}\varepsilon_{YZ}}{\varepsilon_{ZZ}} & -\frac{\varepsilon_{XZ}\sin\alpha}{\varepsilon_{ZZ}} \\ -\frac{\varepsilon_{XZ}\sin\alpha}{\varepsilon_{ZZ}} & 0 & -\frac{\varepsilon_{YZ}\sin\alpha}{\varepsilon_{ZZ}} & 1-\frac{\sin^2\alpha}{\varepsilon_{ZZ}} \\ \varepsilon_{YX} - \frac{\varepsilon_{YZ}\varepsilon_{XZ}}{\varepsilon_{ZZ}} & 0 & \varepsilon_{YY} - \frac{\varepsilon_{YZ}^2}{\varepsilon_{ZZ}} & -\frac{\varepsilon_{YZ}\sin\alpha}{\varepsilon_{ZZ}} \end{pmatrix}, \qquad \text{* MERGEFORMAT (3)}$$

To obtain the Eigenvalues of the matrix **Δ** the following equation must be solved:

$$\mathrm{Det}\left(\mathbf{\Delta}-\gamma\mathbf{I}\right)=0 . \qquad \text{* MERGEFORMAT (4)}$$

This yields a quartic equation in γ, called the Booker quartic,

$$\gamma^4+\alpha_1\gamma^3+\alpha_2\gamma^2+\alpha_3\gamma+\alpha_4=0 . \qquad \text{* MERGEFORMAT (5)}$$

The four solutions of γ are given by,

$$\begin{aligned}
\gamma_1 &= -\tfrac{1}{12}\left(3\alpha_1+\sqrt{3K_4}+\sqrt{6\left(K_5+K_6\right)}\right)\\
\gamma_2 &= -\tfrac{1}{12}\left(3\alpha_1+\sqrt{3K_4}-\sqrt{6\left(K_5+K_6\right)}\right)\\
\gamma_3 &= -\tfrac{1}{12}\left(3\alpha_1-\sqrt{3K_4}+\sqrt{6\left(K_5-K_6\right)}\right),\\
\gamma_4 &= -\tfrac{1}{12}\left(3\alpha_1-\sqrt{3K_4}-\sqrt{6\left(K_5-K_6\right)}\right)
\end{aligned} \qquad \text{* MERGEFORMAT (6)}$$

with the abbreviations:

$$\begin{aligned}
K_1 &= 2\alpha_2^{\,3}-9\alpha_1\alpha_2\alpha_3+27\alpha_3^{\,2}+27\alpha_1^{\,2}\alpha_4-72\alpha_2\alpha_4\\
K_2 &= \alpha_2^{\,2}-3\alpha_1\alpha_3+12\alpha_4\\
K_3 &= (K_1+\sqrt{K_1^2-4K_2^3})^{1/3}\\
K_4 &= 3\alpha_1^{\,2}-8\alpha_2+\frac{4\times 2^{1/3}K_2}{K_3}+2\times 2^{2/3}K_3\\
K_5 &= 3\alpha_1^{\,2}-8\alpha_2-\frac{2\times 2^{1/3}K_2}{K_3}-2^{2/3}K_3\\
K_6 &= \frac{3\sqrt{3}\left(\alpha_1^{\,3}-4\alpha_1\alpha_2+8\alpha_3\right)}{\sqrt{K_4}}
\end{aligned} . \qquad \text{* MERGEFORMAT (7)}$$

Two of the solutions for γ belong to forward traveling waves. For these a positive sign is characteristic if the solutions are real. Otherwise the forward direction is indicated by a positive imaginary part (note that the identification must be repeated separately for each wavelength and each layer!). We denote the two solutions, which belong to forward traveling waves by γ_{+I} and γ_{+II} and the corresponding solutions for backward traveling waves by γ_{-I} and γ_{-II} .

The corresponding Eigenvectors can be determined by putting each γ_i into the homogeneous system of linear equations

$$\begin{pmatrix}\Delta_{11}-\gamma & \Delta_{12} & \Delta_{13} & \Delta_{14}\\ \Delta_{21} & \Delta_{22}-\gamma & \Delta_{23} & \Delta_{24}\\ \Delta_{31} & \Delta_{32} & \Delta_{33}-\gamma & \Delta_{34}\\ \Delta_{41} & \Delta_{42} & \Delta_{43} & \Delta_{44}-\gamma\end{pmatrix}\cdot\begin{pmatrix}\Psi_1\\ \Psi_2\\ \Psi_3\\ \Psi_4\end{pmatrix}=\mathbf{0} . \qquad \text{* MERGEFORMAT (8)}$$

and by solving simultaneously three of the four equations in eqn. * MERGEFORMAT (8). This yields solutions of three components of $\boldsymbol{\Psi}$ in terms of a fourth, which is arbitrary.

The following two solutions for the eigenvectors have been obtained based on Cramer's rule, where the subscripts indicate the choice of the equations from eqn. (15).

$$\boldsymbol{\Psi}_{1,2,3,i} = \begin{pmatrix} \mathrm{Det}\begin{vmatrix} \Delta_{14} & \Delta_{12} & \Delta_{13} \\ \Delta_{24} & \Delta_{22}-\gamma_i & \Delta_{23} \\ \Delta_{34} & \Delta_{32} & \Delta_{33}-\gamma_i \end{vmatrix} \\ \mathrm{Det}\begin{vmatrix} \Delta_{11}-\gamma_i & \Delta_{14} & \Delta_{13} \\ \Delta_{21} & \Delta_{24} & \Delta_{23} \\ \Delta_{31} & \Delta_{34} & \Delta_{33}-\gamma_i \end{vmatrix} \\ \mathrm{Det}\begin{vmatrix} \Delta_{11}-\gamma_i & \Delta_{12} & \Delta_{14} \\ \Delta_{21} & \Delta_{22}-\gamma_i & \Delta_{24} \\ \Delta_{31} & \Delta_{32} & \Delta_{34} \end{vmatrix} \\ \mathrm{Det}\begin{vmatrix} \Delta_{11}-\gamma_i & \Delta_{12} & \Delta_{13} \\ \Delta_{21} & \Delta_{22}-\gamma_i & \Delta_{23} \\ \Delta_{31} & \Delta_{32} & \Delta_{33}-\gamma_i \end{vmatrix} \end{pmatrix}, \boldsymbol{\Psi}_{2,3,4,i} = \begin{pmatrix} \begin{vmatrix} \Delta_{24} & \Delta_{22}-\gamma_i & \Delta_{23} \\ \Delta_{34} & \Delta_{32} & \Delta_{33}-\gamma_i \\ \Delta_{44}-\gamma_i & \Delta_{42} & \Delta_{43} \end{vmatrix} \\ \begin{vmatrix} \Delta_{21} & \Delta_{24} & \Delta_{23} \\ \Delta_{31} & \Delta_{34} & \Delta_{33}-\gamma_i \\ \Delta_{41} & \Delta_{44}-\gamma_i & \Delta_{43} \end{vmatrix} \\ \begin{vmatrix} \Delta_{21} & \Delta_{22}-\gamma_i & \Delta_{24} \\ \Delta_{31} & \Delta_{32} & \Delta_{34} \\ \Delta_{41} & \Delta_{42} & \Delta_{44}-\gamma_i \end{vmatrix} \\ \begin{vmatrix} \Delta_{21} & \Delta_{22}-\gamma_i & \Delta_{23} \\ \Delta_{31} & \Delta_{32} & \Delta_{33}-\gamma_i \\ \Delta_{41} & \Delta_{42} & \Delta_{43} \end{vmatrix} \end{pmatrix}. \text{* MERGEFORMAT}$$

(9)

From the eigenvectors obtained from eqn. * MERGEFORMAT (9), new vectors $\boldsymbol{\Psi}_i$ can be formed by linear combination,

$$\boldsymbol{\Psi}_i = \boldsymbol{\Psi}_{1,2,3,i} + \boldsymbol{\Psi}_{2,3,4,i}, \qquad i = +I,-I,+II,-II, \qquad \text{* MERGEFORMAT (10)}$$

and a matrix $\mathbf{D}_\mathbf{\Psi}$ can be determined, according to

$$\mathbf{D}_\mathbf{\Psi} = \begin{pmatrix} \Psi_{+I,1} & \Psi_{-I,1} & \Psi_{+II,1} & \Psi_{-II,1} \\ \Psi_{+I,2} & \Psi_{-I,2} & \Psi_{+II,2} & \Psi_{-II,2} \\ \Psi_{+I,3} & \Psi_{-I,3} & \Psi_{+II,3} & \Psi_{-II,3} \\ \Psi_{+I,4} & \Psi_{-I,4} & \Psi_{+II,4} & \Psi_{-II,4} \end{pmatrix}. \qquad \text{* MERGEFORMAT (11)}$$

This matrix is called the dynamical matrix. Since backward traveling waves do not exist in the semiinfinite medium *N*+1, $\mathbf{D}_\mathbf{\Psi}(N+1)$ simplifies to

$$\mathbf{D}_\mathbf{\Psi}(N+1) = \begin{pmatrix} \Psi_{+I,1} & 0 & \Psi_{+II,1} & 0 \\ \Psi_{+I,2} & 0 & \Psi_{+II,2} & 0 \\ \Psi_{+I,3} & 0 & \Psi_{+II,3} & 0 \\ \Psi_{+I,4} & 0 & \Psi_{+II,4} & 0 \end{pmatrix}. \qquad \text{* MERGEFORMAT (12)}$$

The four amplitudes A_i of the waves within a layered medium *n* are linked with the amplitudes $A_i(n-1)$ of the medium *n* – 1 at the boundary between medium *n* and *n* – 1 by

$$\begin{pmatrix} A_1(n-1) \\ A_2(n-1) \\ A_3(n-1) \\ A_4(n-1) \end{pmatrix} = \mathbf{D}_\mathbf{\Psi}^{-1}(n-1)\mathbf{D}_\mathbf{\Psi}(n)\mathbf{P}(n)\begin{pmatrix} A_1(n) \\ A_2(n) \\ A_3(n) \\ A_4(n) \end{pmatrix}. \qquad \text{* MERGEFORMAT (13)}$$

The diagonal matrices $\mathbf{P}(n)$ are usually called propagation matrices and are given by

$$\mathbf{P}(n)=\begin{pmatrix} \exp(ik_0 d_n \gamma_{+\mathrm{I}}) & 0 & 0 & 0 \\ 0 & \exp(ik_0 d_n \gamma_{-\mathrm{I}}) & 0 & 0 \\ 0 & 0 & \exp(ik_0 d_n \gamma_{+\mathrm{II}}) & 0 \\ 0 & 0 & 0 & \exp(ik_0 d_n \gamma_{-\mathrm{II}}) \end{pmatrix},$$ * MERGEFORMAT (14)

where d_n represents the layer thickness. By introducing the transfer matrix $\mathbf{T_p}$, the amplitudes of the incident waves and the reflected waves at the interface medium 0 / medium 1 can be linked with the amplitudes of the transmitted waves in the exit medium (N+1) by the equation

$$\begin{pmatrix} A_s \\ B_s \\ A_p \\ B_p \end{pmatrix} = \mathbf{D_\Psi}^{-1}(0)\prod_{n=1}^{N}\mathbf{T_p}(n)\,\mathbf{D_\Psi}(N+1)\begin{pmatrix} C_s \\ 0 \\ C_p \\ 0 \end{pmatrix}.$$ * MERGEFORMAT (15)

Here, the transfer matrix of the nth layer can be calculated by $\mathbf{T_p}(n)=\mathbf{D_\Psi}(n)\mathbf{P}(n)\mathbf{D_\Psi}^{-1}(n)$ and the transfer matrices in the product are ordered according to their Z-coordinates. A_s and A_p represent the amplitudes of the incident waves with s- and p-polarization, and the B_i and C_i are the amplitudes of the reflected and the transmitted waves, respectively.

Finally, we define a matrix $\tilde{\mathbf{M}}$ by the relation

$$\tilde{\mathbf{M}} = \mathbf{D_\Psi}^{-1}(0)\prod_{n=1}^{N}\mathbf{T_p}(n)\,\mathbf{D_\Psi}(N+1).$$ * MERGEFORMAT (16)

$$\begin{pmatrix} A_s \\ B_s \\ A_p \\ B_p \end{pmatrix} = \begin{pmatrix} \tilde{M}_{11} & \tilde{M}_{12} & \tilde{M}_{13} & \tilde{M}_{14} \\ \tilde{M}_{21} & \tilde{M}_{22} & \tilde{M}_{23} & \tilde{M}_{24} \\ \tilde{M}_{31} & \tilde{M}_{32} & \tilde{M}_{33} & \tilde{M}_{34} \\ \tilde{M}_{41} & \tilde{M}_{42} & \tilde{M}_{43} & \tilde{M}_{44} \end{pmatrix}\begin{pmatrix} C_s \\ 0 \\ C_p \\ 0 \end{pmatrix}.$$ * MERGEFORMAT (17)

The reflection and transmission coefficients r_{ss} and t_{ps}, e.g., can then be calculated as follows:

$$\begin{aligned} r_{ss} &= \left(\frac{B_s}{A_s}\right)_{A_p=0} = \frac{\tilde{M}_{21}\tilde{M}_{33}-\tilde{M}_{23}\tilde{M}_{31}}{\tilde{M}_{11}\tilde{M}_{33}-\tilde{M}_{13}\tilde{M}_{31}} \\ t_{ps} &= \left(\frac{C_s}{A_p}\right)_{A_s=0} = \frac{-\tilde{M}_{13}}{\tilde{M}_{11}\tilde{M}_{33}-\tilde{M}_{13}\tilde{M}_{31}} \end{aligned}.$$ * MERGEFORMAT (18)

The first subscript of the coefficients denotes the polarization of the incident wave and the second the orientation of the analyzer, respectively. The corresponding reflectances R_{ij}, where $i,j = s,p$, are obtained by:

$$R_{ij} = \left|r_{ij}\right|^2.$$ * MERGEFORMAT (19)

For the system vacuum/C=O layer/substrate, the dynamical matrices of the scalar media are:

$$\mathbf{D}(vacuum)=\begin{pmatrix}1 & 1 & 0 & 0\\ \cos\alpha & \cos\alpha & 0 & 0\\ 0 & 0 & \cos\alpha & \cos\alpha\\ 0 & 0 & -1 & 1\end{pmatrix}.$$

* MERGEFORMAT (20)

$$\mathbf{D}(Subs)=\begin{pmatrix}1 & 0 & 0 & 0\\ n_{Subs}\cos\beta_{Subs} & 0 & 0 & 0\\ 0 & 0 & \cos\beta_{Subs} & 0\\ 0 & 0 & -n_{Subs} & 0\end{pmatrix}.$$

* MERGEFORMAT (21)

Where $\cos\beta_{Subs}$ is obtained by using Snell's law:

$$\cos\beta_{Subs}=\sqrt{1-\left[\left(1/n_{Subs}\right)\sin\alpha\right]^2}\ .$$

* MERGEFORMAT (22)

As long as the layered medium is uniaxial and oriented with its unique axis along Z, the delta matrix of this medium is given by:

$$\mathbf{\Delta}=\begin{pmatrix}0 & 1 & 0 & 0\\ -\sin^2\alpha+\varepsilon_{XX} & 0 & 0 & 0\\ 0 & 0 & 0 & 1-\frac{\sin^2\alpha}{\varepsilon_{ZZ}}\\ 0 & 0 & \varepsilon_{YY} & 0\end{pmatrix},$$

* MERGEFORMAT (23)

The corresponding dynamical matrix is then determined as:

$$\mathbf{D}(Subs)=\begin{pmatrix}\frac{1}{\sqrt{\sin^2\alpha+\varepsilon_{XX}}} & -\frac{1}{\sqrt{\sin^2\alpha+\varepsilon_{XX}}} & 0 & 0\\ 1 & 1 & 0 & 0\\ 0 & 0 & -\sqrt{\frac{1-\frac{\sin^2\alpha}{\varepsilon_{ZZ}}}{\varepsilon_{YY}}} & \sqrt{\frac{1-\frac{\sin^2\alpha}{\varepsilon_{ZZ}}}{\varepsilon_{YY}}}\\ 0 & 0 & 1 & 1\end{pmatrix}.$$

* MERGEFORMAT (24)

In this case, the 4×4 matrices can be separated into two 2×2 matrices and further simplifications are possible. The reflection coefficient for s- and p-polarized light are then given by:[3]

$$\begin{aligned}
r_s &= \frac{r_{12,s}+r_{23,s}\exp(2i\phi)}{1+r_{12,s}r_{23,s}\exp(2i\phi)}\\
r_{12,s} &= \frac{k_1'-k_2'}{k_1'+k_2'},\ r_{23,s}=\frac{k_2'-k_3'}{k_2'+k_3'}\\
k_1' &= \cos\alpha\\
k_i'(\tilde{\nu}) &= n_i'(\tilde{\nu})\cos\beta_i=\sqrt{n_i'(\tilde{\nu})^2-\sin^2\alpha} \qquad i=2,3\\
n_2'(\tilde{\nu}) &= \sqrt{\varepsilon_{XX}}\\
\phi(\tilde{\nu}) &= 2\pi\tilde{\nu}k_2'(\tilde{\nu})d
\end{aligned}$$

.* MERGEFORMAT (25)

$$
\begin{aligned}
r_p &= \frac{r_{12,p} + r_{23,p}\exp\left(2i\phi\right)}{1 + r_{12,p} r_{23,p}\exp\left(2i\phi\right)} \\
r_{12,p} &= \frac{n_1'^2 k_2' - \sqrt{\varepsilon_{YY}\varepsilon_{ZZ}}\,k_1'}{n_1'^2 k_2' + \sqrt{\varepsilon_{YY}\varepsilon_{ZZ}}\,k_1'}, \; r_{23,p} = \frac{\sqrt{\varepsilon_{YY}\varepsilon_{ZZ}}\,k_3' - n_3'^2 k_2'}{\sqrt{\varepsilon_{YY}\varepsilon_{ZZ}}\,k_3' + n_3'^2 k_2'} \\
k_1' &= n_1' \cos\alpha \\
k_i'\left(\tilde{\nu}\right) &= n_i'\left(\tilde{\nu}\right)\cos\beta_i = \sqrt{n_i'\left(\tilde{\nu}\right)^2 - \sin^2\alpha} \qquad i = 2,3 \\
n_2'\left(\tilde{\nu}\right) &= \sqrt{\varepsilon_{ZZ}} \\
\phi\left(\tilde{\nu}\right) &= 2\pi\tilde{\nu}\sqrt{\frac{\varepsilon_{YY}}{\varepsilon_{ZZ}}}\,k_2'\left(\tilde{\nu}\right)d
\end{aligned}
\qquad .\backslash\text{* MERGEFORMAT (26)}
$$

If we set $\varepsilon_{ZZ} = \varepsilon_{b,\parallel}$ and $\varepsilon_{YY} = \varepsilon_{b,\perp}$, eqn. (0.1) is obtained.

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