Kinetic Theory of Nonequilibrium Alignment Phenomena in Dilute Polyatomic Gases in External Magnetic and Electric Fields

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Z. Naturforsch. **33a**, 761–777 (1978); received June 7, 1978

Dedicated to prof. dr. L. Waldmann on the occasion of his 65th birthday

The inverse operator technique for the solution of the linearized Waldmann-Snider equation in first order Chapman-Enskog-approximation is used to calculate non-equilibrium rotational angular momentum polarizations caused by a temperature- or a velocity gradient. The presence of an external homogeneous magnetic or electric field is taken into account. In particular, the viscomagnetic vector- and tensor polarization for linear molecules and the thermoelectric vector- and tensor polarization for polar symmetric top molecules are treated. Detailed expressions are given in terms of Waldmann-Snider collision cross sections. While for the tensor polarizations the self-adjoint part of the collision operator gives the major contribution, the vector polarizations occur due to the existence of a non-selfadjoint part.

I. Introduction

The state of a dilute monatomic gas is described by the one-particle distribution function $f(t, \boldsymbol{x}, \boldsymbol{c})$ where t is the time, $\boldsymbol{x}$ is the position and $\boldsymbol{c}$ is the molecular velocity. For a polyatomic gas, however, the distribution function depends also on the internal rotational and vibrational degrees of freedom. While the vibration does not play any role for most gases at room temperature, the rotation is always important. Thus the distribution function depends on the molecular rotational angular momentum $\hbar \boldsymbol{J}$ as well, i.e. it is a density matrix with respect to magnetic quantum numbers. Its temporal behavior is governed by the Waldmann-Snider equation [1, 2] which treats the molecular collision in a fully quantum mechanical way: the Waldmann-Snider collision term contains the binary scattering matrix and its adjoint rather than a differential cross section.

Because of its $\boldsymbol{J}$-dependence, the Waldmann-Snider collision operator contains all information needed for the description of the alignment of $\boldsymbol{J}$ caused by macroscopic gradients. The most general alignment phenomena occurring are non-equilibrium velocity-rotational angular momentum correlations, e.g. $\langle \boldsymbol{c} \times \boldsymbol{J} \rangle$ (the bracket $\langle \cdots \rangle$ denotes a non-equilibrium average). In this paper, however, restriction is made to the treatment of two simple kinds of polarization, viz. the vector polarization $\langle \boldsymbol{J} \rangle$ and the tensor polarization $\langle \overline{\boldsymbol{JJ}} \rangle$ (the bar $\overline{}$ denotes the symmetric traceless part of a tensor). Both are of particular interest since they give directly rise to macroscopically observable effects: With the vector polarization a magnetization $\boldsymbol{M}$ of the gas is connected; e.g. for a gas of linear diamagnetic molecules this magnetization is given by

$$\boldsymbol{M} = n\, \mu_n\, g \,\langle \boldsymbol{J} \rangle\,, \tag{1.1}$$

where n is the particle number density, μ_n is the nuclear magneton and g is the molecular g-factor.

The occurrence of a tensor polarization $\langle \overline{\boldsymbol{JJ}} \rangle$ (or more exactly: of a weighted tensor polarization $\langle \overline{\boldsymbol{JJ}}/(J^2 - \frac{3}{4}) \rangle$) causes birefringence in a gas of optically anisotropic molecules: The tensor polarization is connected with the anisotropic part of the dielectric tensor by [3]

$$\overline{\boldsymbol{\epsilon}} = -\,2\pi\, n\,(\alpha_\parallel - \alpha_\perp)\,\langle J^2/(J^2 - \tfrac{3}{4}) \rangle_0^{1/2} \cdot \langle \overline{\boldsymbol{JJ}}/(J^2 - \tfrac{3}{4}) \rangle\,, \tag{1.2}$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the molecular polarizabilities parallel and perpendicular to the figure axis of the molecule and where $\langle \cdots \rangle_0$ denotes an equilibrium average.

By the way, the existence of $\langle \overline{\boldsymbol{JJ}} \rangle$ influences the momentum transport in the gas and thus the viscosity. This can be observed by applying a constant magnetic field which causes a precession of the tensor polarization. The viscosity becomes

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a field dependent 4th rank tensor (Senftleben-Beenakker effect [4]); the relative change of the viscosity in a magnetic field can be measured very accurately [5].

A non-equilibrium situation in a pure gas can be brought about by a temperature gradient $\boldsymbol{\nabla} T$ or by a velocity gradient $\overline{\boldsymbol{\nabla v}}$. First, some phenomenological considerations concerning the connection of vector- and tensor polarization with those gradients are in order. Here, only effects due to first order derivatives are studied, the Burnett type alignment effects (e.g. a tensor polarization proportional to $\overline{\boldsymbol{\nabla\nabla}} T$ which has been treated by Hess [6]) are disregarded. All effects of interest are summarized in Table 1.

Table 1. The various effects Λ^{Ll}.

Polarization and macroscopic observable	$\boldsymbol{\nabla} T$	$\overline{\boldsymbol{\nabla v}}$
$<\boldsymbol{J}>$ magnetization	$\boldsymbol{\Lambda}^{11}(E \neq 0)$	$\boldsymbol{\Lambda}^{12}(H \neq 0)$
$<\overline{\boldsymbol{JJ}}>$ birefringence	$\boldsymbol{\Lambda}^{21}(E \neq 0)$	$\boldsymbol{\Lambda}^{22}$

Let us first consider a gas under the influence of a temperature gradient: Since $\boldsymbol{\nabla} T$ is a polar vector and $\boldsymbol{J}$ is an axial one, a temperature gradient cannot (without an external field) give rise to a vector polarization. The presence of a magnetic field which is also an axial vector does not alter this statement. However, in a gas of polar molecules under the influence of an electric field $\boldsymbol{E}$, a $\langle \boldsymbol{J} \rangle$-polarization can exist. From reasons of rotational and parity symmetry the constitutive law is (see Table 1)

$$\langle \boldsymbol{J} \rangle = \alpha \boldsymbol{E} \times \boldsymbol{\nabla} T \,, (\boldsymbol{\Lambda}^{11}) \,, \tag{1.3}$$

where the scalar coefficient α can still depend on E^2.

There can also be a thermo-electric tensor polarization in a polar gas, given by

$$\langle \overline{\boldsymbol{JJ}} \rangle = \alpha_1 \overline{\boldsymbol{E \nabla}} T + \alpha_2 \overline{\boldsymbol{EE}}\, \boldsymbol{E} \cdot \boldsymbol{\nabla} T, (\boldsymbol{\Lambda}^{21}) \,. \tag{1.4}$$

Here, α_1 and α_2 are again functions of E^2 (see Table 1). The thermo-electric tensor polarization gives rise to a birefringence linear in $\boldsymbol{\nabla} T$ in the bulk of the gas. In the boundary layer between a polyatomic gas and a solid, however, such an effect can exist without an electric field [7].

For a viscous streaming gas with $\overline{\boldsymbol{\nabla v}} \neq 0$, similar arguments hold: The vector polarization $\langle \boldsymbol{J} \rangle$ which has the same parity as $\overline{\boldsymbol{\nabla v}}$ is connected to this quantity by a 3rd rank tensor. Without external fields, $\langle \boldsymbol{J} \rangle$ and $\overline{\boldsymbol{\nabla v}}$ cannot be connected because of the Curie principle. A viscous flow can give rise to a vector polarization only in the presence of an external field. The constitutive law in a magnetic field $\boldsymbol{H} = H \boldsymbol{h}$ can be written as (see Table 1)

$$\langle \boldsymbol{J} \rangle = \boldsymbol{\beta}(\boldsymbol{H}) \cdot (\boldsymbol{h} \cdot \overline{\nabla \boldsymbol{v}}), (\boldsymbol{\Lambda}^{12}) \,, \tag{1.5}$$

with the second rank tensor

$$\boldsymbol{\beta}(\boldsymbol{H}) = \beta^{\parallel} \boldsymbol{h}\boldsymbol{h} + \beta^{\perp}(\boldsymbol{\delta} - \boldsymbol{h}\boldsymbol{h}) + \beta^{\mathrm{tr}}\, \boldsymbol{\epsilon} \cdot \boldsymbol{h} \,. \tag{1.6}$$

In Eq. (1.6), $\boldsymbol{\delta}$ and $\boldsymbol{\epsilon}$ are the isotropic 2nd- and 3rd rank tensors, respectively, the coefficients $\beta^{\parallel}$, $\beta^{\perp}$ and β^{tr} still depend on the magnitude H of the magnetic field and vanish for $H = 0$. In the presence of an electric field in a polar gas one obtains analogous expressions to Eqs. (1.5) and (1.6), however $\beta^{\mathrm{tr}} = 0$. A kinetic theory of the viscomagnetic vector polarization for linear molecules with special stress on the transverse effect has previously been given by Köhler [8] who used the moment equations pertaining to the linearized Waldmann-Snider equation.

It should be noted here, that also without external fields a vector polarization can occur due to a curl of the velocity field

$$\langle \boldsymbol{J} \rangle = \alpha_{\mathrm{B}} \operatorname{rot} \boldsymbol{v} \,. \tag{1.7}$$

This Barnett effect, however, is usually some orders of magnitude smaller than the effects mentioned above and will be disregarded here.

Since the tensor polarization $\langle \overline{\boldsymbol{JJ}} \rangle$ and $\overline{\boldsymbol{\nabla v}}$ have the same parity and tensor rank they are connected even without the presence of external fields (see Table 1):

$$\langle \overline{\boldsymbol{JJ}} \rangle = \beta\, \overline{\boldsymbol{\nabla v}}, (\boldsymbol{\Lambda}^{22}) \,. \tag{1.8}$$

Equation (1.8) inserted into Eq. (1.2) yields the relation between $\overline{\boldsymbol{\epsilon}}$ and $\overline{\boldsymbol{\nabla v}}$, i.e. the phenomenon of flow birefringence in molecular gases which has first been proposed by Hess [3] in 1969 and which has been measured by Baas [9]. In the presence of external fields, Eq. (1.8) becomes

$$\langle \overline{\boldsymbol{JJ}} \rangle = \boldsymbol{\beta}(\boldsymbol{E}, \boldsymbol{H}) : \overline{\boldsymbol{\nabla v}} \,, \tag{1.9}$$

where $\boldsymbol{\beta}(\boldsymbol{E}, \boldsymbol{H})$ is a fourth rank tensor. This tensor has recently been calculated for a polar gas of symmetric top molecules in perpendicular electric and magnetic fields by Köhler [10]. The influence of a magnetic field on flow birefringence has been studied theoretically [11] but still has to be verified experimentally.

It is a question of particular interest how these alignment effects are related to the molecular interaction. In a collision a purely spherical interaction cannot affect the molecular rotational angular momentum. Thus all alignment effects are crucially dependent on the nonsphericity of the potential and provide an important tool for the investigation of these noncentral forces.

It is the purpose of the kinetic theory of polyatomic gases based on the Waldmann-Snider equation to obtain expressions for the phenomenologically introduced coefficients α, α_1, α_2, β, $\beta^{\|}$, $\beta^{\perp}$, β^{tr} and $\boldsymbol{\beta}$ in terms of properties of single molecules (e.g. magnetic or electric dipole moments) and their mutual nonspherical interaction or scattering amplitude, respectively [12].

The paper proceeds as follows: In Section II, general expressions for the coefficients relating the angular momentum polarizations to the temperature- and velocity gradients are derived. In Sect. III, properties of the pertaining magnetic (Zeeman-) and electric (Stark-) field Liouville operators for the precessional motions are discussed, in particular their behavior under parity and time reversal. In Sect. IV, the usual inverse operator technique [13] as previously used for the calculation of magnetic-field-dependent transport coefficients [14] will be applied to the calculation of J-polarizations. In Sects. V and VI, the theory is applied to the calculation of the viscomagnetic vector- and tensor polarization in gases of linear diamagnetic molecules and to the thermo-electric vector- and tensor polarization in polar gases of symmetric top molecules. The respective polarization production coefficients are given in terms of effective Waldmann-Snider collision cross sections and precession angles. It is shown that for the vector polarization the non-selfadjoint part of the Waldmann-Snider collision operator is important (i.e. an odd number of collision integrals with Onsager-Casimir symmetry $L_{ij} = -L_{ji}$ occurs), while for the tensor polarization an even number of collision brackets with Onsager-Casimir symmetry occurs apart from the brackets with the usual Onsager symmetry ($L_{ij} = L_{ji}$). In Sect. VII it is shown that with a modified form of the inverse operator technique a more straightforward derivation of the polarization production coefficients is achieved.

II. General Expressions for Non-Equilibrium Angular Momentum Polarizations

We consider a dilute gas of diamagnetic symmetric top molecules. The state of the gas will be described by the one-particle distribution operator

$$f(t, \boldsymbol{x}, \boldsymbol{c}, \boldsymbol{J}, J_{\|}),$$

where t is the time, $\boldsymbol{x}$ is the position, $\boldsymbol{c}$ is the molecular velocity, $\boldsymbol{J}$ is the dimensionless molecular rotational angular momentum and $J_{\|}$ is its component along the figure axis of the molecule ($J_{\|} = 0$ for linear molecules). The nonequilibrium average $\langle \overline{J_{\mu_1} \dots J_{\mu_L}} \rangle$ defines the L-th rank tensor polarization where

$$\langle \cdots \rangle = \frac{1}{n} \operatorname{Tr} \int \mathrm{d}^3 c (\cdots) f, \tag{2.1}$$

and where the bar $\overline{}$ refers to the symmetric traceless part of a tensor. In Eq. (2.1), "Tr" denotes the sum over j and K quantum numbers ($j(j+1)$ is the eigenvalue of J^2 and K is the eigenvalue of $J_{\|}$) as well as the trace over magnetic quantum numbers; $n = \operatorname{Tr} \int \mathrm{d}^3 c f$ is the particle number density. For the distribution operator the usual ansatz

$$\begin{aligned} & f(t, \boldsymbol{x}, \boldsymbol{c}, \boldsymbol{J}, J_{\|}) \\ &\quad = f_0(t, \boldsymbol{x}, \boldsymbol{c}, J^2, J_{\|})(1 + \varphi(t, \boldsymbol{x}, \boldsymbol{c}, \boldsymbol{J}, J_{\|})) \end{aligned} \tag{2.2}$$

is made, where the local equilibrium distribution f_0 is given by

$$f_0 = n Z_{\mathrm{rot}}^{-1} \left(\frac{2\pi k_{\mathrm{B}} T}{m} \right)^{-3/2} \cdot \exp\left[-\frac{m(\boldsymbol{c} - \boldsymbol{v})^2}{2 k_{\mathrm{B}} T} - \frac{H_{\mathrm{rot}}}{k_{\mathrm{B}} T} \right]. \tag{2.3}$$

Here

$$H_{\mathrm{rot}} = \frac{\hbar^2 J^2}{2\Theta_{\perp}} + \frac{\hbar^2 J_{\|}^2}{2\Theta_{\|}} \left(1 - \frac{\Theta_{\|}}{\Theta_{\perp}} \right)$$

is the internal rotational Hamiltonian for a symmetric top molecule and

$$Z_{\mathrm{rot}} = \operatorname{Tr} \exp(-H_{\mathrm{rot}}/k_{\mathrm{B}} T)$$

is the rotational partition function.

From reasons to be seen later it is more convenient to use the spherical tensor notation than the Cartesian one; J^L_M $(-L \leqq M \leqq L)$ then denotes the spherical tensor equivalent to the Cartesian tensor $\overline{J_{\mu_1} \dots J_{\mu_L}}$. The properly normalized polarization tensor proportional to J^L_M is denoted by $\Phi(\boldsymbol{J})^L_M$. The normalization condition is

$$\langle [\Phi(\boldsymbol{J})^L_M]^\dagger \, \Phi(\boldsymbol{J})^{L'}_{M'} \rangle_0 = \delta_{LL'} \, \delta_{MM'} \, , \tag{2.4}$$

where $\langle \cdots \rangle_0$ means an equilibrium average and the adjoint of a spherical tensor is

$$[\Phi^L_M]^\dagger = (-1)^M \, \Phi^L_{-M} \, .$$

Since without fields there is no equilibrium polarization, one has for $L \neq 0$

$$\langle \Phi(\boldsymbol{J})^L_M \rangle = \frac{1}{n} \operatorname{Tr} \int \mathrm{d}^3 c \, \Phi(\boldsymbol{J})^L_M \, f_0 \, \varphi \, . \tag{2.5}$$

The relative deviation of the distribution operator from equilibrium obeys the linearized Waldmann-Snider equation [1, 2]. In the Chapman-Enskog version, this equation reads

$$(R + i \, \mathscr{L}) \, \varphi = - \, \psi \, , \tag{2.6}$$

where R is the linearized Waldmann-Snider collision operator containing the binary scattering matrix and its adjoint and $\mathscr{L}$ is the Liouville operator governing the free precessional motion of $\boldsymbol{J}$ in a homogenous magnetic or electric field. The distribution φ may be written as a sum

$$\varphi = \varphi^{(1)} + \varphi^{(2)} + \cdots$$

according to the orders in Chapman-Enskog approximation; the same holds for the inhomogeneity term ψ. Since we restrict ourselves here to first-order Chapman-Enskog effects, we will omit the superscript "(1)" in the following treatment. The inhomogeneity ψ can be expressed in terms of scalar products of two forces and fluxes as [14]

$$\psi = \frac{1}{n} \sum_{l=1}^{2} \sum_{m=-l}^{l} (Q^l_m)^* \, F^l_m \, . \tag{2.7}$$

Here, the driving force for the heat conduction is given by

$$F^1_m = \nabla_m \ln T \tag{2.8}$$

and the flux Q^1_m then takes the form

$$Q^1_m = \left(\frac{2 k_\mathrm{B} T}{m} \right)^{1/2} \left(W^2 - \frac{5}{2} + \varepsilon - \langle \varepsilon \rangle_0 \right) W^1_m \, . \tag{2.9}$$

Its average is proportional to the heat flux; $W = (m/2 k_\mathrm{B} T)^{1/2} \, (\boldsymbol{c} - \boldsymbol{v})$ is the peculiar molecular velocity and ε is the internal rotational energy divided by $k_\mathrm{B} T$. For the viscosity the driving force is the velocity gradient

$$F^2_m = [\nabla v]^2_m \tag{2.10}$$

and

$$Q^2_m = 2 \, W^2_m \tag{2.11}$$

the average of which is proportional to the friction pressure tensor.

In a Hilbert space formulation one has

$$\langle \Phi(\boldsymbol{J})^L_M \rangle^* = \langle (\Phi(\boldsymbol{J})^L_M)^\dagger \rangle \equiv \langle\langle \Phi(\boldsymbol{J})^L_M \, | \, \varphi \rangle\rangle \, , \tag{2.12}$$

where $\langle\langle \cdots | \cdots \rangle\rangle$ denotes a scalar product in Hilbert space (see Equation (3.9)). With the formal solution of Eq. (2.6),

$$\varphi = - \, (R + i \, \mathscr{L})^{-1} \, \psi \, , \tag{2.13}$$

one obtains with the help of Eqs. (2.7), (2.12)

$$n \, \langle \Phi(\boldsymbol{J})^L_M \rangle = - \sum_{lm} \langle\langle \Phi(\boldsymbol{J})^L_M \, | \, (R + i \, \mathscr{L})^{-1} \, Q^l_m \rangle\rangle_0{}^* \, F^l_m \, , \quad l = 1, 2 \, . \tag{2.14}$$

The bracket

$$\Lambda^{Ll}_{Mm} \equiv \langle\langle \Phi(\boldsymbol{J})^L_M \, | \, (R + i \, \mathscr{L})^{-1} \, Q^l_m \rangle\rangle^* \, , \quad L, l = 1, 2 \tag{2.15}$$

of the super-operator $(R + i \mathscr{L})^{-1}$ is called "polarization production coefficient" because it states how much $\langle J^L_M \rangle$ polarization is produced in the gas by the F^l_m-force. The calculation of the four coefficients $\boldsymbol{\Lambda}^{11}$, $\boldsymbol{\Lambda}^{21}$, $\boldsymbol{\Lambda}^{12}$ and $\boldsymbol{\Lambda}^{22}$ is the purpose of this paper! From the rotational invariance of the collision operator follows that Λ^{Ll}_{Mm} is proportional to $\delta_{Ll} \, \delta_{Mm}$ if no external field is present $(\mathscr{L} = 0)$ and the parity invariance of R requires that $\langle J^L_M \rangle$ and F^l_m have the same parity. With external fields, however, these arguments are no longer valid, e.g. there is only invariance for rotations about the field axis. For Λ^{Ll}_{Mm} one has the relation

$$\Lambda^{Ll*}_{Mm} = (-1)^{M+m} \, \Lambda^{Ll}_{-M-m} \, . \tag{2.16}$$

Since F^l_m is either the temperature- or the velocity gradient, Eq. (2.14) is the starting point for the kinetic treatment of all thermo-electric or visco-magnetic polarization phenomena. Although we will not discuss the more general case of non-equilibrium velocity-angular momentum correlations,

$$\langle [\Phi^{pq}(\boldsymbol{W}, \boldsymbol{J})]^L_M \rangle = \sum_{m,s} \sqrt{2L+1}\,(-1)^{p+q-M} \begin{pmatrix} p & q & L \\ m & s & -M \end{pmatrix} \cdot \langle \Phi(\boldsymbol{W})^p_m \, \Phi(\boldsymbol{J})^q_s \rangle \,, \tag{2.17}$$

this case is also contained in Equation (2.14). Here $[\Phi^{pq}(\boldsymbol{W}, \boldsymbol{J})]^L_M]$ is a spherical tensor constructed by coupling of a spherical tensor in $\boldsymbol{W}$ of rank p with a spherical tensor in $\boldsymbol{J}$ of rank q to give a compound spherical tensor of rank L, c.f. [15]; the quantity $\begin{pmatrix} p & q & L \\ m & s & -M \end{pmatrix}$ denotes a $3j$-symbol [16]. For $p=1$, $q=2$ one has the Kagan polarization which plays an important role for the Senftleben-Beenakker effect of heat conductivity [4, 19].

III. Magnetic- and Electric Field Liouville Operators

In this section, properties of Liouville operators [17] governing the free precessional motion of molecular magnetic- or electric dipole moments in homogeneous external magnetic and electric fields, respectively, are discussed. For reasons of simplicity the discussion is restricted to linear diamagnetic molecules for the magnetic field Liouville operator and to polar symmetric top molecules in the case of the electric field Liouville operator.

1. Definitions

The Zeeman Liouville operator describing the free precessional motion of the molecular magnetic dipole moment $\boldsymbol{\mu}_{\mathrm{m}}$ in a magnetic field $\boldsymbol{H}$ is defined by

$$\mathscr{L}(\boldsymbol{H}) = -\frac{1}{n\,\hbar}\,[\boldsymbol{\mu}_{\mathrm{m}} \cdot \boldsymbol{H},]_- \,, \tag{3.1}$$

where n is the particle number density. The corresponding Stark Liouville operator for an electric dipole moment $\boldsymbol{\mu}_{\mathrm{e}}$ in an electric field $\boldsymbol{E}$ is

$$\mathscr{L}(\boldsymbol{E}) = -\frac{1}{n\,\hbar}\,[\boldsymbol{\mu}_{\mathrm{e}} \cdot \boldsymbol{E},]_- \,. \tag{3.2}$$

For linear diamagnetic molecules the magnetic moment is

$$\boldsymbol{\mu}_{\mathrm{m}} = \mu_{\mathrm{n}}\, g\, \boldsymbol{J} \,, \tag{3.3}$$

where μ_{n} is the nuclear magneton and g is the g factor. For these molecules Eq. (3.1) becomes then

$$\mathscr{L}(\boldsymbol{H}) = -\frac{1}{n}\,\omega_{\mathrm{H}}[\boldsymbol{h} \cdot \boldsymbol{J},]_- \tag{3.4}$$

with $\boldsymbol{H} = H\,\boldsymbol{h}$ and

$$\omega_{\mathrm{H}} = \mu_{\mathrm{n}}\, g\, H/\hbar \tag{3.5}$$

being the Larmor frequency*.

For polar symmetric top molecules the electric dipole moment can be written as

$$\boldsymbol{\mu}_{\mathrm{e}} = \mu_{\mathrm{e}}\, \boldsymbol{u} \,, \tag{3.6}$$

where $\boldsymbol{u}$ is a unit vector along the direction of the figure axis. If only matrix elements of $\boldsymbol{u}$ diagonal in rotational quantum numbers, $\boldsymbol{u}^{jj}$, are considered, this diagonal part of $\boldsymbol{u}$ can be represented also by $\boldsymbol{J}$ as [18]

$$\boldsymbol{u}_{\mathrm{d}} = \boldsymbol{J} J_{\|}/J^2 \tag{3.6}$$

where $J_{\|} = \boldsymbol{J} \cdot \boldsymbol{u}$. The elements of $\boldsymbol{u}$ nondiagonal in rotational quantum numbers lead to a second order Stark contribution which is usually neglected if there is a first order Stark contribution. Only for linear molecules this second order contribution becomes decisive for the Senftleben-Beenakker effects [18]. Notice that $J_{\|}$ commutes with any space-fixed component of $\boldsymbol{J}$. Because of (3.6), the Stark Liouville operator for symmetric top molecules in an electric field $\boldsymbol{E} = E\,\boldsymbol{e}$ is given by

$$\mathscr{L}(\boldsymbol{E}) = -\frac{1}{n}\,\omega_{\mathrm{E}}[\boldsymbol{e} \cdot \boldsymbol{J} J_{\|}/J^2,]_- \tag{3.7}$$

with

$$\omega_{\mathrm{E}} = \mu_{\mathrm{e}}\, E/\hbar \,. \tag{3.8}$$

For the evaluation of the field term in Eqs. (3.4), (3.7) we will need the commutation relation

$$[J_z, J^q_\mu]_- = \mu\, J^q_\mu \,.$$

For the following considerations it is useful to introduce a Hilbert space notation. The elements of the Hilbert space are the operators $\varphi(\boldsymbol{J})$, $\psi(\boldsymbol{J}) \ldots$, and a scalar product is defined by

$$\langle\langle \Phi | \psi \rangle\rangle = \frac{1}{n}\,\mathrm{Tr} \int \mathrm{d}^3 c\, \Phi^\dagger f_0\, \psi \,. \tag{3.9}$$

It has the properties

$$\langle\langle \Phi | \psi \rangle\rangle = \langle\langle \psi | \Phi \rangle\rangle^* , \quad \langle\langle \Phi | \Phi \rangle\rangle \geqq 0 \,. \tag{3.10}$$

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* For symmetric top molecules (3.3) is valid if g is replaced by an approximate

$$g_{\mathrm{eff}} = g_\perp \left(1 + \frac{g_{\|} - g_\perp}{g_\perp} \left\langle \frac{J_{\|}^2}{J^2} \right\rangle_0 \right).$$

An operator acting on the elements of the Hilbert space (which are operators) is called superoperator, an example of which is the Liouville operator. The adjoint of the Liouville superoperator, $\mathscr{L}^{\#}$, is defined by

$$\langle\langle \Phi | \mathscr{L} \psi \rangle\rangle \equiv \langle\langle \mathscr{L}^{\#} \Phi | \psi \rangle\rangle \,. \tag{3.11}$$

With the help of Eqs. (3.1), (3.2) one finds

$$(\mathscr{L}^{\#} \Phi)^{\dagger} = - \mathscr{L} \Phi^{\dagger} = (\mathscr{L} \Phi)^{\dagger} \tag{3.12}$$

from which, in turn, $\mathscr{L}^{\#} = \mathscr{L}$ is inferred, i.e. $\mathscr{L}$ is self-adjoint. As the quantity $i\mathscr{L}$ occurs in Eq. (2.6) it is practical to introduce $\hat{\mathscr{L}} = i\mathscr{L}$.

2. *Behavior under Parity*

The parity superoperator $\mathbb{P}$ is defined by

$$\mathbb{P}\Phi \equiv P\Phi P^{-1} \equiv \Phi_P \,,$$

where P is the common parity operator acting on states; e.g. one has $P\boldsymbol{J}P^{-1} = \boldsymbol{J}$. For the scalar product (3.9) parity invariance requires

$$\langle\langle \Phi | \psi \rangle\rangle = \langle\langle \mathbb{P}\Phi | \mathbb{P}\psi \rangle\rangle \equiv \langle\langle \Phi_P | \psi_P \rangle\rangle \,. \tag{3.13}$$

Notice, that $\mathbb{P}$ acts only on the microscopic variables of the system such as $\boldsymbol{c}$, $\boldsymbol{J}$, $\boldsymbol{\mu}_{\mathrm{m}}$, $\boldsymbol{\mu}_{\mathrm{e}}$ and not on the fields (cf. [17]). From Eq. (3.13) follows

$$\begin{aligned} \langle\langle \Phi | \hat{\mathscr{L}} \psi \rangle\rangle &= \langle\langle \mathbb{P}\Phi | \mathbb{P} \hat{\mathscr{L}} \mathbb{P}^{-1} \mathbb{P} \psi \rangle\rangle \\ &= \langle\langle \Phi_P | \hat{\mathscr{L}}_P \psi_P \rangle\rangle \end{aligned} \tag{3.14}$$

with $\hat{\mathscr{L}}_P = \mathbb{P} \hat{\mathscr{L}} \mathbb{P}^{-1}$. From Eqs. (3.1,2) it is easily seen that

$$\begin{aligned} \hat{\mathscr{L}}_P(\boldsymbol{H}) &= \hat{\mathscr{L}}(\boldsymbol{H}), \\ \hat{\mathscr{L}}_P(\boldsymbol{E}) &= \hat{\mathscr{L}}(-\boldsymbol{E}) = -\hat{\mathscr{L}}(\boldsymbol{E}) \,. \end{aligned} \tag{3.15}$$

If two operators Φ and ψ are "eigenoperators" of the superoperator $\mathbb{P}$, i.e. $\mathbb{P}\Phi = P_{\Phi}\Phi$, $\mathbb{P}\psi = P_{\psi}\psi$, P_{Φ}, $P_{\psi} = \pm 1$, Eq. (3.14) yields

$$\begin{aligned} &\langle\langle \Phi | \hat{\mathscr{L}}(\boldsymbol{H}) \psi \rangle\rangle \\ &\quad = P_{\Phi} P_{\psi} \langle\langle \Phi | \hat{\mathscr{L}}(\boldsymbol{H}) \psi \rangle\rangle \,, \end{aligned} \tag{3.16}$$

$$\begin{aligned} &\langle\langle \Phi | \hat{\mathscr{L}}(\boldsymbol{E}) \psi \rangle\rangle \\ &\quad = - P_{\Phi} P_{\psi} \langle\langle \Phi | \hat{\mathscr{L}}(\boldsymbol{E}) \psi \rangle\rangle \,. \end{aligned} \tag{3.17}$$

Thus the magnetic Liouville operator only connects operators with the same parity ($P_{\Phi} P_{\psi} = +1$) while the electric field Liouville operator only connects those with opposite parity ($P_{\Phi} P_{\psi} = -1$).

3. *Behavior under Time Reversal*

If $\mathbb{T}$ is the time reversal superoperator acting on the microscopic variables (not on the fields!), time reversal invariance requires the relation

$$\langle\langle \mathbb{T}\Phi | \mathbb{T}\psi \rangle\rangle = \langle\langle \psi | \Phi \rangle\rangle = \langle\langle \Phi | \psi \rangle\rangle^{*} \tag{3.18}$$

for any Φ, ψ. Then for a bracket of the Liouville operator follows

$$\langle\langle \Phi | \hat{\mathscr{L}} \psi \rangle\rangle = \langle\langle \hat{\mathscr{L}}_T \psi_T | \Phi_T \rangle\rangle \tag{3.19}$$

with $\hat{\mathscr{L}}_T = \mathbb{T} \hat{\mathscr{L}} \mathbb{T}^{-1}$. Direct inspection of $\hat{\mathscr{L}}_T \Phi_T$ for

$$\hat{\mathscr{L}}(\boldsymbol{E}, \boldsymbol{H}) \equiv \hat{\mathscr{L}}(\boldsymbol{E}) + \hat{\mathscr{L}}(\boldsymbol{H})$$

yields

$$\hat{\mathscr{L}}_T(\boldsymbol{E}, \boldsymbol{H}) = \hat{\mathscr{L}}(-\boldsymbol{E}, \boldsymbol{H}) \,. \tag{3.20}$$

On the other hand, $\hat{\mathscr{L}}^{\#}(\boldsymbol{E}, \boldsymbol{H}) = \hat{\mathscr{L}}(-\boldsymbol{E}, -\boldsymbol{H})$ is valid and

$$\hat{\mathscr{L}}_T(\boldsymbol{E}, \boldsymbol{H}) = \hat{\mathscr{L}}^{\#}(\boldsymbol{E}, -\boldsymbol{H}) \tag{3.21}$$

holds. Therefore for brackets of the electric and magnetic field Liouville operators the following respective relations are valid:

$$\begin{aligned} \langle\langle \Phi | \hat{\mathscr{L}}(\boldsymbol{E}) \psi \rangle\rangle &= \langle\langle \psi_T | \hat{\mathscr{L}}^{\#}_{T}(\boldsymbol{E}) \Phi_T \rangle\rangle \\ &= - \langle\langle \Phi_T | \hat{\mathscr{L}}(\boldsymbol{E}) \psi_T \rangle\rangle^{*} \,, \end{aligned} \tag{3.22}$$

$$\begin{aligned} \langle\langle \Phi | \hat{\mathscr{L}}(\boldsymbol{H}) \psi \rangle\rangle &= \langle\langle \psi_T | \hat{\mathscr{L}}^{\#}_{T}(\boldsymbol{H}) \Phi_T \rangle\rangle \\ &= \langle\langle \Phi_T | \hat{\mathscr{L}}(\boldsymbol{H}) \psi_T \rangle\rangle^{*} \,. \end{aligned} \tag{3.23}$$

For Hermition operators Φ, ψ, the brackets (3.22), (3.23) are real. If Φ and ψ show a definite behavior under time reversal ($\mathbb{T}\Phi = T_{\Phi}\Phi$, $\mathbb{T}\psi = T_{\psi}\psi$, T_{Φ}, $T_{\psi} = \pm 1$) one obtains

$$\begin{aligned} \langle\langle \Phi | \hat{\mathscr{L}}(\boldsymbol{E}) \psi \rangle\rangle &= - T_{\Phi} T_{\psi} \langle\langle \Phi | \hat{\mathscr{L}}(\boldsymbol{E}) \psi \rangle\rangle \,, \\ \langle\langle \Phi | \hat{\mathscr{L}}(\boldsymbol{H}) \psi \rangle\rangle &= T_{\Phi} T_{\psi} \langle\langle \Phi | \hat{\mathscr{L}}(\boldsymbol{H}) \psi \rangle\rangle \,. \end{aligned} \tag{3.24}$$

Equation (3.24) tells that $\hat{\mathscr{L}}(\boldsymbol{E})$ only connects quantities with different behavior under time reversal while $\hat{\mathscr{L}}(\boldsymbol{H})$ only connects those with equal behavior. Of course, this is also true for the non-Hermitian spherical tensor operators φ^{L}_{M}, ψ^{L}_{M} since their components can always be written as a linear combination of components of the corresponding Hermitian Cartesian tensor operators.

4. *General Onsager Relations*

Finally, the Onsager relations for transport coefficients in electric and magnetic fields are derived. Due to the time reversal invariance of the molecular interaction, the linearized Waldmann-Snider collision operator fulfils the relation

$$R_T = \mathbb{T}\, R\, \mathbb{T}^{-1} = R^{\#}\,. \tag{3.25}$$

Notice, however, that in contrast to the linearized Boltzmann collision operator the Waldmann-Snider collision operator is, in general, not self-adjoint, i.e. $R^{\#} \neq R$. For collision brackets then one has

$$\begin{aligned}\langle\langle \Phi \,|\, R\,\psi \rangle\rangle &= \langle\langle R_T\,\psi_T \,|\, \Phi_T \rangle\rangle \\ &= \langle\langle \psi_T \,|\, R\,\Phi_T \rangle\rangle\,. \end{aligned}\tag{3.26}$$

Combining Eqs. (3.22), (3.23) and (3.26) we find for Hermitian Φ, ψ

$$\begin{aligned}&\langle\langle \Phi \,|\, (R + \hat{\mathscr{L}}(\boldsymbol{E}, \boldsymbol{H}))\,\psi \rangle\rangle \\ &\quad= \langle\langle \psi_T \,|\, (R + \hat{\mathscr{L}}(\boldsymbol{E}, -\boldsymbol{H}))\,|\, \Phi_T \rangle\rangle\,. \end{aligned}\tag{3.27}$$

If a generalized transport coefficient $\Lambda_{\Phi\psi}$ is defined by the corresponding bracket of the inverse operator $(R + \hat{\mathscr{L}}(\boldsymbol{E}, \boldsymbol{H}))^{-1}$ (e.g. for $\Phi = \psi =$ heat flux or friction pressure tensor the usual heat conductivity or viscosity in electric and magnetic fields is treated), Eq. (3.27) yields the generalized Onsager relations

$$\begin{aligned}\Lambda_{\Phi\psi}(\boldsymbol{E}, \boldsymbol{H}) &= \langle\langle \Phi \,|\, (R + \hat{\mathscr{L}}(\boldsymbol{E}, \boldsymbol{H}))^{-1}\,\psi \rangle\rangle \\ &= \langle\langle \psi_T (R + \hat{\mathscr{L}}(\boldsymbol{E}, -\boldsymbol{H}))^{-1} \,|\, \Phi_T \rangle\rangle \\ &= \Lambda_{\psi_T \Phi_T}(\boldsymbol{E}, -\boldsymbol{H})\,. \end{aligned}\tag{3.28}$$

If Φ and ψ show the same behavior under time reversal, the generalized Onsager relations

$$\Lambda_{\Phi\psi}(\boldsymbol{E}, \boldsymbol{H}) = +\,\Lambda_{\psi\Phi}(\boldsymbol{E}, -\boldsymbol{H}) \tag{3.29}$$

hold. If they have not the same behavior under time reversal, one has the Onsager-Casimir relations

$$\Lambda_{\Phi\psi}(\boldsymbol{E}, \boldsymbol{H}) = -\,\Lambda_{\psi\Phi}(\boldsymbol{E}, -\boldsymbol{H})\,. \tag{3.30}$$

IV. Inverse Operator Technique (Standard Form)

In order to obtain a more detailed form of the polarization production coefficient Eq. (2.15), i.e. a representation in terms of Waldmann-Snider collision integrals and precession angles, the inverse operator technique [13] will be applied which has previously been used for the calculation of the magnetic field influence on transport properties [14, 15].

Let us first introduce a complete set S of expansion tensors $\varphi^{pqrst}(\boldsymbol{W}, \boldsymbol{J}, J_{\|})$, where p and q denote the tensorial rank in $\boldsymbol{W}$ and $\boldsymbol{J}$, respectively, r, s, t the orders of Sonine polynomials in W^2, generalized Wang-Chang-Uhlenbeck-de Boer polynomials in J^2 and polynomials in $J_{\|}$. For the set $\{r, s, t\}$ sometimes the collective index α will be used. The complete set S is subdivided into two disjunct subsets S_1 and S_2 where S_1 contains all tensors with $q = 0$ ($\boldsymbol{J}$-independent expansion tensors) and S_2 contains the $\boldsymbol{J}$-dependent ones ($q \neq 0$). A nexample is given in Table 2. According to this decomposition also the collision operator is split:

$$R = R_{\mathrm{d}} \oplus R_{\mathrm{nd}}\,, \tag{4.1}$$

where R_{d} acts within S_1 or S_2 and R_{nd} couples S_1 and S_2. An alternative way of splitting R can lead to a somewhat simpler approach as it will be discussed in Section VII.

Table 2. Set of orthonormal tensors Φ^{pqrst} used in Chapters V—VIII; p denotes the tensorial rank in $\boldsymbol{W}$, q the tensorial rank in $\boldsymbol{J}$; r denotes the order in W^2, s the order in $\varepsilon = H_{\mathrm{rot}}/k_{\mathrm{B}}\,T$ and t the order in $J_{\|}$.

$$\left.\begin{aligned}\Phi^{10100} &= \left(\frac{4}{5}\right)^{1/2} \boldsymbol{W} \left(\frac{5}{2} - W^2\right) \\ \Phi^{10010} &= \left(\frac{2\,k_{\mathrm{B}}}{c_{\mathrm{rot}}}\right)^{1/2} \boldsymbol{W}\,(\varepsilon - \langle\varepsilon\rangle_0) \\ \boldsymbol{\Phi}^{20000} &= \sqrt{2}\;\overline{\boldsymbol{W}\boldsymbol{W}} \end{aligned}\right\} S_1$$

$$\left.\begin{aligned}\Phi^{01000} &= \sqrt{3}\,\langle J^2\rangle_0^{-1/2}\,\boldsymbol{J} \\ \Phi^{01001} &= \sqrt{3}\,\langle J_{\|}^2\,J^2\rangle_0^{-1/2}\,J_{\|}\,\boldsymbol{J} \\ \boldsymbol{\Phi}^{02000} &= \left(\frac{15}{2}\right)^{1/2} \left\langle J^2 \left(J^2 - \frac{3}{4}\right)\right\rangle_0^{-1/2} \overline{\boldsymbol{J}\boldsymbol{J}} \\ \boldsymbol{\Phi}^{02001} &= \left(\frac{15}{2}\right)^{1/2} \left\langle J_{\|}^2\,J^2 \left(J^2 - \frac{3}{4}\right)\right\rangle_0^{-1/2} J_{\|}\;\overline{\boldsymbol{J}\boldsymbol{J}} \\ \boldsymbol{\Phi}^{12000} &= \sqrt{2}\;\boldsymbol{W}\,\boldsymbol{\Phi}^{02000} \\ \boldsymbol{\Phi}^{12001} &= \sqrt{2}\;\boldsymbol{W}\,\boldsymbol{\Phi}^{02001} \\ \boldsymbol{\Phi}^{21000} &= \sqrt{2}\;\overline{\boldsymbol{W}\boldsymbol{W}}\,\boldsymbol{\Phi}^{01000}\,. \end{aligned}\right\} S_2\,.$$

Since matrix elements of R_{nd} are nonzero only if the intermolecular potential is nonspherical and usually the nonspherical part of the potential is small compared to the spherical part, an expansion of the inverse operator $(R + i\,\mathscr{L})^{-1}$ in powers of R_{nd} is practical. With

$$\tilde{R}_{\mathrm{d}} = R_{\mathrm{d}} + i\,\mathscr{L} \tag{4.2}$$

one obtains

$$\begin{aligned}(R + i\,\mathscr{L})^{-1} &= \tilde{R}_{\mathrm{d}}^{-1} - \tilde{R}_{\mathrm{d}}^{-1}\,R_{\mathrm{nd}}\,\tilde{R}_{\mathrm{d}}^{-1} \\ &\quad + \tilde{R}_{\mathrm{d}}^{-1}\,R_{\mathrm{nd}}\,\tilde{R}_{\mathrm{d}}^{-1}\,R_{\mathrm{nd}}\,\tilde{R}_{\mathrm{d}}^{-1} - \cdots\,. \end{aligned}\tag{4.3}$$

While the first term of the r.h.s. of Eq. (4.3) determines the isotropic values of the transport coefficients and the third term describes the field influence on the transport properties [14], it is the second term which contributes in lowest order to the production of non-equilibrium angular momentum polarizations. From Eqs. (4.3) and (2.15) together with the use of complete sets one finds for the polarization production coefficient

$$\begin{aligned}\Lambda^{Ll}_{Mm} &= -\langle\langle \Phi(\boldsymbol{J})^L_M \,|\, \tilde{R}_\mathrm{d}^{-1}\, R_\mathrm{nd}\, \tilde{R}_\mathrm{d}^{-1}\, Q^l_M \rangle\rangle^* \\ &= -\sum_{pq\alpha L'p'\alpha'} \langle\langle \Phi(\boldsymbol{J})^L_M \,|\, \tilde{R}_\mathrm{d}^{-1} [\Phi^{pq\alpha}]^{L'}_{M'} \rangle\rangle^* \\ &\quad \cdot \langle\langle [\Phi^{pq\alpha}]^{L'}_{M'} \,|\, R_\mathrm{nd}\, \Phi^{p'0\alpha'}_{m'} \rangle\rangle^* \\ &\quad \cdot \langle\langle \Phi^{p'0\alpha'}_{m'} \,|\, R_\mathrm{d}^{-1}\, Q^l_m \rangle\rangle \,, \end{aligned} \tag{4.4}$$

where $[\Phi^{pq\alpha}]^L_M$ has been defined in Equation (2.17). Due to the rotational invariance of the collision operator one has

$$\begin{aligned}&\langle\langle \Phi^{p'0\alpha'}_{m'} \,|\, R_\mathrm{d}^{-1}\, Q^l_m \rangle\rangle \\ &\quad = \delta_{lp'}\, \delta_{mm'} (2l+1)^{-1} \langle\langle \boldsymbol{\Phi}^{l0\alpha'} | \cdot R_\mathrm{d}^{-1}\, \boldsymbol{Q}^l \rangle\rangle \,,\end{aligned} \tag{4.5}$$

where the dot denotes a contraction over all tensor indices. Likewise one has

$$\begin{aligned}&\langle\langle [\Phi^{pq\alpha}]^{L'}_{M'} \,|\, R_\mathrm{nd}\, \Phi^{p'0\alpha'}_{m'} \rangle\rangle \\ &\quad = i^{p+q-p'}\, \delta_{L'p'}\, \delta_{M'm'}\, v_\mathrm{rel}\, \overline{\mathfrak{S}}\left(\begin{smallmatrix} pq\alpha \\ p'0\alpha' \end{smallmatrix}\right)_{L'}\end{aligned} \tag{4.6}$$

with

$$v_\mathrm{rel} = \sqrt{16 k_\mathrm{B} T / \pi m} \tag{4.7}$$

and $\overline{\mathfrak{S}}\left(\begin{smallmatrix} pq\alpha \\ p'0\alpha' \end{smallmatrix}\right)_{L'}$ being an effective Waldmann-Snider cross section [20, 21]*. These effective cross sections are the same as those defined in Ref. [15] (see also Section VII). Finally, for elements involving the external field which occurs in $\tilde{R}_\mathrm{d}^{-1}$, invariance with respect to rotations about this axis holds. With the field direction as z-axis one has

$$\begin{aligned}&\langle\langle \Phi(\boldsymbol{J})^L_M \,|\, \tilde{R}_\mathrm{d}^{-1} [\Phi^{pq\alpha}]^{L'}_{M'} \rangle\rangle^* \\ &\quad = \delta_{MM'} \{\tilde{R}_\mathrm{d}^{-1*}(p\,q\,\alpha)\}^{LL'}_M \,,\end{aligned} \tag{4.8}$$

where $\{\tilde{R}_\mathrm{d}^{-1}\}^{LL'}_M$ is the $L-L'$ matrix element of the inverse matrix $\tilde{R}_\mathrm{d}^{-1}$. This element has to be calculated within a suitable set of expansion tensors from S_2. For this calculation also the matrix elements of the Liouville operator in Eq. (3.4) or (3.7) are needed which are

$$\begin{aligned}&\langle\langle \Phi^{pq\alpha}_{MN} \,|\, \mathscr{L}(\boldsymbol{H}) \,|\, \Phi^{p'q'\alpha'}_{M'N'} \rangle\rangle \\ &\quad = -N\, \omega_\mathrm{H}\, n^{-1}\, \delta_{pp'}\, \delta_{qq'}\, \delta_{\alpha\alpha'}\, \delta_{MM'}\, \delta_{NN'}\end{aligned} \tag{4.9}$$

and

$$\begin{aligned}&\langle\langle \Phi^{pq\alpha}_{MN} \,|\, \mathscr{L}(\boldsymbol{E}) \Phi^{p'q'\alpha'}_{M'N'} \rangle\rangle \\ &\quad = -N\, \omega_\mathrm{E}\, n^{-1}\, \delta_{pp'}\, \delta_{qq'}\, \Delta(\alpha, \alpha')\, \delta_{MM'}\, \delta_{NN'} \,.\end{aligned} \tag{4.10}$$

Here α, α' denote again sets $\{r, s, t\}$, $\{r', s', t'\}$ and $\Delta(\alpha, \alpha')$ is zero unless $r = r'$, $s = s'$ and $\Delta t = \pm 1$. The polarization production coefficient (4.4) can with Eqs. (4.5)—(4.8) be written as

$$\begin{aligned}\Lambda^{Ll}_{Mm} &= -\frac{v_\mathrm{rel}}{2l+1}\, \delta_{Mm} \sum_{pq\alpha\alpha'} \{\tilde{R}_\mathrm{d}^{-1*}(p\,q\,\alpha)\}^{Ll}_M \\ &\quad \cdot i^{l-p-q}\, \overline{\mathfrak{S}}\left(\begin{smallmatrix} pq\alpha \\ l0\alpha' \end{smallmatrix}\right)_l \langle\langle \boldsymbol{\Phi}^{l0\alpha'} | \cdot R_\mathrm{d}^{-1}\, \mathbf{Q}^l \rangle\rangle ; \\ &\qquad l = 1, 2 \,.\end{aligned} \tag{4.11}$$

Since Λ^{Ll}_{Mm} is diagonal in M-indices, it is sufficient to write Λ^{Ll}_M instead of Λ^{Ll}_{MM}. The production coefficient of $\boldsymbol{J}$-polarizations is essentially determined by the nonspherical part of the molecular interaction since the cross section $\overline{\mathfrak{S}}\left(\begin{smallmatrix} pq\alpha \\ l0\alpha' \end{smallmatrix}\right)_l$ vanishes for a purely spherical potential [21, 22]. Via the collision bracket $\langle\langle \boldsymbol{\Phi}^{l0\alpha'} | \cdot R_\mathrm{d}^{-1}\, \mathbf{Q}^l \rangle\rangle$ an isotropic transport coefficient enters. Once more it should be stressed that without external electric or magnetic fields one has $L = l$ and polarization and force $\mathbf{F}^l$ have the same parity. Thus, without external fields, e.g., a vector polarization cannot be produced by a temperature- or velocity gradient.

V. Viscomagnetic Vector- and Tensor Polarization in Gases of Linear Molecules

In this section, the tensor- and vector polarizations produced in a viscous flow ($\overline{\boldsymbol{\nabla v}} \neq 0$) of polyatomic gases in the presence of a magnetic field $\boldsymbol{H} = H\boldsymbol{h}$ are treated (effects $\boldsymbol{\Lambda}^{22}$ and $\boldsymbol{\Lambda}^{12}$ of Table 1). As the essential features can be illustrated for a gas of linear diamagnetic molecules, we will only treat this simple case and not the somewhat more involved of symmetric top molecules in magnetic or electric fields. Starting point is the Equation (4.11). Since it is the simpler effect, the tensor polarization is treated first.

1. *Viscomagnetic Tensor Polarization* $\boldsymbol{\Lambda}^{22}$

For the calculation of the tensor polarization $\langle\overline{\boldsymbol{JJ}}\rangle$ produced by $\overline{\boldsymbol{\nabla v}}$, we have to put $L = l = 2$ in Eq. (4.11) and

$$\mathbf{Q}^2 = 2\,\mathbf{W}^2 = \sqrt{2}\, \boldsymbol{\Phi}^{20} \,.$$

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* The bar over the $\mathfrak{S}$ expresses the fact that $\boldsymbol{W}$ and $\boldsymbol{J}$ on one side of the collision operator are first coupled together.

The possible branches which lead to a $\overline{\boldsymbol{JJ}}$ polarization starting with a $\overline{\boldsymbol{WW}}$ polarization via collisions and precessions are shown in the first diagram:

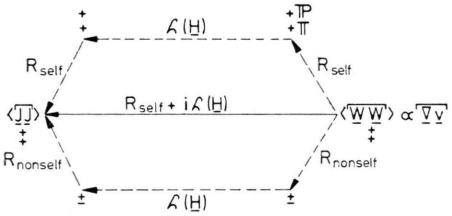

Fig. 1. Schematic diagram for the possible branches which lead to a $\overline{\boldsymbol{JJ}}$-polarization in a viscous flow.

The signs $\overset{+}{+}$ etc. refer to the behavior of the corresponding expansion tensor under parity ℙ and time reversal 𝕋. The full line denotes the direct collisional coupling of $\overline{\boldsymbol{WW}}$ and $\overline{\boldsymbol{JJ}}$. The dashed lines represent paths involving intermediate expansion tensors. In the upper one, the self-adjoint part of the collision operator occurs twice, in the lower one the nonselfadjoint part occurs twice.

The simplest approximation consists in taking into account only the direct coupling and neglecting the dashed parts which are of higher order in nonsphericity. Then one simply takes $q=2$, $p=\alpha=0$ in Eq. (4.11). If the α-indices (which are dummy ones here) are dropped for simplicity, the production coefficient of the tensor polarization is obtained as

$$A^{22}_{M} = -\sqrt{2}\,\frac{v_{\text{rel}}}{5}\,\{\tilde{R}_{\text{d}}^{-1*}(02)\}^{22}_{M}\,\mathfrak{S}\binom{02}{20} \cdot \langle\langle \boldsymbol{\Phi}^{20} | : R_{\text{d}}^{-1}\,\boldsymbol{\Phi}^{20}\rangle\rangle\,. \tag{5.1}$$

The isotropic value of the viscosity is given by

$$\eta = \frac{k_{\text{B}}T}{5}\langle\langle \boldsymbol{\Phi}^{20} | : R_{\text{d}}^{-1}\,\boldsymbol{\Phi}^{20}\rangle\rangle\,,$$

and in lowest order in nonsphericity the matrix $\tilde{R}_{\text{d}}(02)$ can be replaced by its (02)—(02)-element. Observing Eq. (4.9) we find

$$\{\tilde{R}_{\text{d}}^{-1*}(02)\}^{22}_{M} = [v_{\text{rel}}\,\mathfrak{S}(02)\,(1+i\,M\,\varphi_{02}]^{-1}\,, \tag{5.2}$$

where

$$\varphi_{02} = \omega_{\text{H}}/n\,v_{\text{rel}}\,\mathfrak{S}(02)$$

is an effective precession angle. Thus the spherical components of the viscomagnetic tensor polarization are given by ($P = n\,k_{\text{B}}T$ is the pressure and $\boldsymbol{J}^2 = \sqrt{2/15}\,\langle J^2(J^2-\tfrac{3}{4})\rangle_0^{\frac{1}{2}}\,\boldsymbol{\Phi}(\boldsymbol{J})^2$)

$$\langle \Phi(\boldsymbol{J})^2_M\rangle = \frac{\sqrt{2}}{P}\,\eta\,\frac{\mathfrak{S}\binom{02}{20}}{\mathfrak{S}(02)}\,(1+i\,M\,\varphi_{02})^{-1}\,[\boldsymbol{\nabla v}]^2_M\,. \tag{5.3}$$

For zero magnetic field one has $\varphi_{02}=0$, for high magnetic fields the tensor components with $M \neq 0$ are averaged out because of the fast precession. The Cartesian tensor equivalent of Eq. (5.3) is

$$\langle \overline{\boldsymbol{JJ}}\rangle = \frac{2}{\sqrt{15}}\,\langle J^2(J^2-\tfrac{3}{4})\rangle_0^{\frac{1}{2}}\,\frac{\mathfrak{S}\binom{02}{20}}{\mathfrak{S}(02)} \cdot \frac{\eta}{P}\sum_{M=-2}^{2}\mathscr{P}^{(M)}(\boldsymbol{h})\,(1+i\,M\,\varphi_{02})^{-1} : \overline{\boldsymbol{\nabla v}}\,. \tag{5.4}$$

Here, the $\mathscr{P}^{(M)}(\boldsymbol{h})$ are 4th rank projection tensors [22] built up from second rank projection tensors $\mathbf{P}^{(m)}(\boldsymbol{h})$ by means of

$$\mathscr{P}^{(M)}(\boldsymbol{h}) = \sum_{m_1,\,m_2}\delta_{M,\,m_1+m_2}\,\mathbf{P}^{(m_1)}(\boldsymbol{h})\,\mathbf{P}^{(m_2)}(\boldsymbol{h})\,, \tag{5.5}$$

where

$$\mathbf{P}^{(0)}(\boldsymbol{h}) = \boldsymbol{h}\,\boldsymbol{h}\,,$$
$$\mathbf{P}^{\pm 1}(\boldsymbol{h}) = \tfrac{1}{2}(\boldsymbol{\delta} - \boldsymbol{h}\,\boldsymbol{h} \mp i\,\boldsymbol{\epsilon}\cdot\boldsymbol{h})\,. \tag{5.6}$$

The connection of $\langle\overline{\boldsymbol{JJ}}\rangle$ (or better $\langle\overline{\boldsymbol{JJ}}/(J^2-\tfrac{3}{4})\rangle$) with the anisotropic part of the dielectric tensor $\overline{\boldsymbol{\epsilon}}$ has been explained by Eq. (1.2); Eq. (5.4) then yields the magnetic field influence on flow birefringence which had earlier been studied with a different method [11].

Both the coupling cross section $\mathfrak{S}\binom{02}{20}$ and the relaxation cross section $\mathfrak{S}(02)$ vanish unless the molecular interaction is nonspherical. Moreover, it can be shown in a first order DWBA treatment [12, 21] that only energetically inelastic collisions contribute to $\mathfrak{S}\binom{02}{20}$.

2. *The Viscomagnetic Vector Polarization* $\boldsymbol{\Lambda}^{12}$

In contradistinction to the viscomagnetic tensor polarization there is no viscomagnetic vector polarization for zero magnetic field. The simplest coupling mechanisms leading to $\langle\boldsymbol{J}\rangle$ are illustrated in the following diagram:

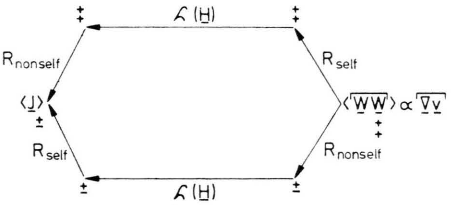

Fig. 2. Schematic diagram for the possible branches which lead to a $\boldsymbol{J}$-polarization in a viscous flow.

Both branches contain the non-selfadjoint part of the collision operator once. The viscomagnetic vector polarization is thus an important tool for the investigation of the non-selfadjoint part of the Waldmann-Snider collision operator.

In the expression for the polarization production coefficient, (4.11) $L=1$, $l=2$ have to be taken. If we use the lower branch of the diagram, the simplest contribution is due to $p=2$, $q=1$, $\alpha=\alpha'=0$ in Eq. (4.11), other contributions being negligible. The upper branch would atl east require $p=q=2$ which is of higher tensorial rank and known to be unimportant from the Senftleben-Beenakker effect of the viscosity [4, 5]. The branch chosen also corresponds to the earlier treatment of the effect with the moment method [8].

Equation (4.11) then yields for the production coefficient of the vector polarization

$$\Lambda_M^{12} = -i\,\frac{\sqrt{2}}{5}\,v_{\text{rel}}\,\{\tilde{R}_{\text{d}}^{-1*}(21)\}_M^{12}\,\overline{\mathfrak{S}}\tbinom{21}{20} \cdot \langle\langle \boldsymbol{\Phi}^{20} | : R_{\text{d}}^{-1}\,\boldsymbol{\Phi}^{20}\rangle\rangle\,. \tag{5.7}$$

The matrix $\{\tilde{R}_{\text{d}}^{*}(21)\}_M$ has to be evaluated with a suitable set of expansion tensors. As the simplest set which is possible we choose the vector $\boldsymbol{\Phi}^{01}$ and the three irreducible components of the 3rd rank tensor $\boldsymbol{\Phi}^{21}$. Using the methods developed in Ref. [15], we obtain the following 4×4 matrix:

$$\{\tilde{R}_{\text{d}}^{*}(21)\}_M \triangleq v_{\text{rel}}\,\mathfrak{S}(21)\begin{pmatrix} 1+i\,\varphi_{21}\,F_M^{11} & i\,\varphi_{21}\,F_M^{12} & 0 & -\overline{\mathfrak{S}}\tbinom{21}{01}/\mathfrak{S}(21) \\ i\,\varphi_{21}\,F_M^{12} & 1+i\,\varphi_{21}\,F_M^{22} & i\,\varphi_{21}\,F_M^{23} & 0 \\ 0 & i\,\varphi_{21}\,F_M^{23} & 1+i\,\varphi_{21}\,F_M^{33} & 0 \\ -\overline{\mathfrak{S}}\tbinom{21}{01}/\mathfrak{S}(21) & \boxed{0} & 0 & \dfrac{(1+i\,M\varphi_{01})\,\mathfrak{S}(01)}{\mathfrak{S}(21)} \end{pmatrix} \tag{5.8}$$

The $2-4$ element of the inverse matrix is needed in Eq. (5.7). In Eq. (5.8), the effective precession angles

$$\varphi_{01} = \omega_{\text{H}}/n\,v_{\text{rel}}\,\mathfrak{S}(01)\,,$$
$$\varphi_{21} = \omega_{\text{H}}/n\,v_{\text{rel}}\,\mathfrak{S}(21) \tag{5.9}$$

have been introduced. For the relaxation cross sections of the three irreducible parts of $\boldsymbol{\Phi}^{21}$ we have used the spherical approximation [15]

$$\overline{\mathfrak{S}}(21)_1 = \overline{\mathfrak{S}}(21)_2 = \overline{\mathfrak{S}}(21)_3 \equiv \mathfrak{S}(21)\,.$$

The coefficients $F_M^{ll'}$ are [15]

$$F_M^{ll'}(p,q) = F_M^{l'l}(p,q) = (-1)^{p+q+l+l'} \cdot [(2l+1)(2l'+1)(2q+1)\,q(q+1)]^{\frac{1}{2}} \cdot (-1)^M \begin{pmatrix} l & l' & 1 \\ -M & M & 0 \end{pmatrix} \begin{Bmatrix} l & l' & 1 \\ q & q & p \end{Bmatrix}, \tag{5.10}$$

where $\begin{pmatrix} l & l' & 1 \\ -M & M' & 0 \end{pmatrix}$ is a $3j$-symbol and $\begin{Bmatrix} l & l' & 1 \\ q & q & p \end{Bmatrix}$ is a $6j$-symbol [16] and where in our case $p=2$, $q=1$. Neglecting $\overline{\mathfrak{S}}\tbinom{21}{01}^2$ as compared to $\mathfrak{S}(01)\times\mathfrak{S}(21)$, we obtain the desired element of the inverse matrix as

$$\{\tilde{R}_{\text{d}}^{-1*}(21)\}_M^{12} = i\left(\frac{3(4-M^2)}{20}\right)^{\frac{1}{2}} \frac{\overline{\mathfrak{S}}\tbinom{01}{21}}{v_{\text{rel}}\,\mathfrak{S}(01)\,\mathfrak{S}(21)} \cdot \frac{\varphi_{21}\left(1+i\,M\left(\dfrac{\varphi_{21}}{3}-\varphi_{01}\right)+\dfrac{M^2}{3}\,\varphi_{01}\,\varphi_{21}\right)}{(1+\varphi_{21}^2)(1+M^2\,\varphi_{01}^2)}\,. \tag{5.11}$$

The elements with $M=\pm 2$ vanish as is expected. The spherical components of the viscomagnetic vector polarization are then given by

$$\langle J_0^1\rangle = \frac{1}{P}\left(\frac{2}{5}\,\langle J^2\rangle_0\right)^{\frac{1}{2}}\eta\,\frac{\overline{\mathfrak{S}}\tbinom{01}{21}\,\overline{\mathfrak{S}}\tbinom{21}{20}}{\mathfrak{S}(01)\,\mathfrak{S}(21)} \cdot \frac{\varphi_{21}}{1+\varphi_{21}^2}\,[\nabla v]_0^2\,, \tag{5.12}$$

$$\langle J_{\pm1}^1\rangle = -\frac{1}{P}\left(\frac{3}{10}\,\langle J^2\rangle_0\right)^{\frac{1}{2}}\eta\,\frac{\overline{\mathfrak{S}}\tbinom{01}{21}\,\overline{\mathfrak{S}}\tbinom{21}{20}}{\mathfrak{S}(01)\,\mathfrak{S}(21)} \cdot \frac{\varphi_{21}\left(1\pm i\left(\dfrac{\varphi_{21}}{3}-\varphi_{01}\right)+\dfrac{1}{3}\,\varphi_{01}\,\varphi_{21}\right)}{(1+\varphi_{01}^2)(1+\varphi_{21}^2)}\,[\nabla v]_{\pm1}^2\,, \tag{5.13}$$

where we have used $J_M^1 = (1/\sqrt{3})\,\langle J^2\rangle_0^{\frac{1}{2}}\,\Phi(\boldsymbol{J})_M^1$.

The connection of spherical and Cartesian vector components is after Edmonds' Equation (5.1.3) [16]

$$A_z = A_0\,,\quad A_x = \frac{1}{\sqrt{2}}\,(A_{-1}-A_{+1}),$$
$$A_y = \frac{i}{\sqrt{2}}\,(A_{-1}+A_{+1}); \tag{5.14}$$
$$A_0 = A_z,\quad A_{\pm1} = \mp\frac{(A_x \pm i\,A_y)}{\sqrt{2}}\,.$$

The corresponding relation between the relevant components of the velocity gradient tensor is

$$[\nabla v]^2_0 = \sqrt{\frac{3}{2}}\,\frac{\partial v_z}{\partial z}\,, \tag{5.15}$$

$$[\nabla v]^2_{\pm 1} = \mp\frac{1}{2}\left(\frac{\partial v_z}{\partial x}+\frac{\partial v_x}{\partial z}\right)-\frac{i}{2}\left(\frac{\partial v_z}{\partial y}+\frac{\partial v_y}{\partial z}\right).$$

With the help of Eqs. (5.14), (5.15), (5.6) the coefficients $\beta^{\parallel}$, $\beta^{\perp}$ and β^{tr} of Eq. (1.6) can be inferred as

$$\beta^{\parallel} = \sqrt{\frac{3}{5}}\,\langle J^2\rangle_0^{\frac{1}{2}}\,\frac{\eta}{P}\,\frac{\overline{\mathfrak{S}}\binom{01}{21}\,\overline{\mathfrak{S}}\binom{21}{20}}{\mathfrak{S}(01)\,\mathfrak{S}(21)}\,\frac{\varphi_{21}}{1+\varphi_{21}^2}\,, \tag{5.16}$$

$$\beta^{\perp} = -\frac{1+\frac{1}{3}\varphi_{01}\varphi_{21}}{1+\varphi_{01}^2}\,\beta_{\parallel}\,,\quad \beta^{\mathrm{tr}} = -\frac{\varphi_{01}-\frac{1}{3}\varphi_{21}}{1+\varphi_{01}^2}\,\beta_{\parallel}\,. \tag{5.17}$$

Of particular interest is the transverse effect: For a flow pattern $\boldsymbol{v} = v(z)\,\boldsymbol{e}_x$ (as it exists in a rectangular channel with gas flow in x-direction and dimensions $L_x, L_y \gg L_z$) and magnetic field $\boldsymbol{H}$ pointing in z-direction, the transverse component of the viscomagnetic vector polarization is

$$\langle J_y\rangle = -\frac{1}{2}\,\beta^{\mathrm{tr}}\,\frac{\partial v_x}{\partial z}\,. \tag{5.18}$$

It vanishes for small and high magnetic fields and reaches its maximum value for

$$\varphi_{21} = (\mathfrak{S}(01)/\mathfrak{S}(21))^{\frac{1}{2}}\,.$$

An estimate of the order of magnitude of the effect for N_2 can be found in Ref. [8]. Finally it should be mentioned that the cross sections $\overline{\mathfrak{S}}\binom{21}{20}$, $\overline{\mathfrak{S}}\binom{01}{21}$ and $\mathfrak{S}(01)$ are crucially dependent on the nonsphericity of the interaction; the occurrence of the non-selfadjoint part of the collision operator manifests itself in the Onsager-Casimir relation $\overline{\mathfrak{S}}\binom{21}{20} = -\,\overline{\mathfrak{S}}\binom{20}{21}$.

VI. Thermoelectric Vector- and Tensor Polarization in Gases of Polar Symmetric Top Molecules

In this section, the vector- and tensor polarization produced in heat conducting polar gases in the presence of an external homogeneous electric field $\boldsymbol{E}$ are studied (effects $\boldsymbol{\Lambda}^{11}$ and $\boldsymbol{\Lambda}^{21}$ of Table 1). Restriction is made to the case of symmetric top molecules where the component of $\boldsymbol{J}$ along the symmetry axis, $J_{\parallel}$, is a good quantum number.

1. Thermoelectric Vector Polarization $\boldsymbol{\Lambda}^{11}$

For the production of the thermoelectric vector polarization one has the following diagram:

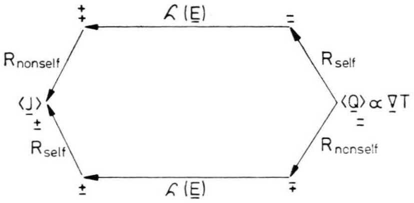

Fig. 3. Schematic diagram for the possible branches which lead to a $\boldsymbol{J}$-polarization in a heat flow.

Here, $\boldsymbol{Q}$ denotes the heat flux. Each branch involves the non-selfadjoint part of the collision operator once. In the expression for the production coefficient, Eq. (4.11), one has $L = l = 1$. For the lower branch, the simplest choice for p, q, α, α' obviously is $p = 0$, $q = 1$, $\alpha = \{r, s, t\} = \{0, 0, 1\}$ and $\alpha' = \{1, 0, 0\}$ and $\{0, 1, 0\}$. Thus the following expression is obtained:

$$\begin{aligned}\Lambda^{11}_M = -\frac{v_{\mathrm{rel}}}{3}\,&\{\tilde{R}_{\mathrm{d}}^{-1*}(01)\}^{11}_M\\ &\cdot\left\{\overline{\mathfrak{S}}\binom{01001}{10100}\langle\langle\boldsymbol{\Phi}^{10100}|\cdot R_{\mathrm{d}}^{-1}\,\boldsymbol{Q}\rangle\rangle\right.\\ &\left.+\,\overline{\mathfrak{S}}\binom{01001}{10010}\langle\langle\boldsymbol{\Phi}^{10010}|\cdot R_{\mathrm{d}}^{-1}\,\boldsymbol{Q}\rangle\rangle\right\}.\end{aligned} \tag{6.1}$$

In Eq. (6.1), the average of

$$\begin{aligned}\boldsymbol{Q} &= \left(\frac{2k_{\mathrm{B}}T}{m}\right)^{\frac{1}{2}}\left(W^2-\frac{5}{2}+\varepsilon-\langle\varepsilon\rangle_0\right)\boldsymbol{W}\\ &= \left(\frac{k_{\mathrm{B}}T}{m}\right)^{\frac{1}{2}}\left(-\sqrt{\frac{5}{2}}\,\boldsymbol{\Phi}^{10100}+\sqrt{\frac{c_{\mathrm{rot}}}{k_{\mathrm{B}}}}\,\boldsymbol{\Phi}^{10010}\right)\end{aligned} \tag{6.2}$$

is the total heat flux and c_{rot} is the rotational heat capacity per molecule. The isotropic heat conductivity

$$\lambda = \frac{k_{\mathrm{B}}}{3}\langle\langle\boldsymbol{Q}|\cdot R_{\mathrm{d}}^{-1}\,\boldsymbol{Q}\rangle\rangle\,,$$

can, after (6.2) be split into a "translational" and a "rotational" part which are defined by

$$\lambda_{\mathrm{transl}} \equiv -\frac{k_{\mathrm{B}}}{3}\left(\frac{5k_{\mathrm{B}}T}{2m}\right)^{\frac{1}{2}}\cdot\langle\langle\boldsymbol{\Phi}^{10100}|\cdot R_{\mathrm{d}}^{-1}\,\boldsymbol{Q}\rangle\rangle\,, \tag{6.3}$$

$$\lambda_{\mathrm{rot}} \equiv \frac{k_{\mathrm{B}}}{3}\left(\frac{c_{\mathrm{rot}}T}{m}\right)^{\frac{1}{2}}\cdot\langle\langle\boldsymbol{\Phi}^{10010}|\cdot R_{\mathrm{d}}^{-1}\,\boldsymbol{Q}\rangle\rangle\,. \tag{6.4}$$

The simplest set for the evaluation of $\{\tilde{R}_{\mathrm{d}}^{-1}(01)\}_M^{11}$ consist of the vector polarization $\propto \boldsymbol{\Phi}^{01000} \propto \boldsymbol{J}$ and the vector polarization $\propto \boldsymbol{\Phi}^{01001} \propto \boldsymbol{J} J_{\|}$. Using

$$\langle\langle \Phi_M^{01001} \,|\, \mathscr{L}(\boldsymbol{E}) \Phi_{M'}^{01000} \rangle\rangle = - M\, \omega_{\mathrm{E}} \frac{f}{n}\, \delta_{MM'}\,, \quad (6.5)$$

$$f \equiv \langle J_{\|}{}^2\rangle_0 / (\langle J^2 J_{\|}{}^2\rangle_0 \, \langle J^2\rangle_0)^{1/2} \quad (6.6)$$

one obtains for the relevant matrix

$$\{\tilde{R}_{\mathrm{d}}^{*}(01)\}_M^{11} \triangleq \begin{pmatrix} v_{\mathrm{rel}}\, \mathfrak{S}(01000) & i\, M\, \omega_{\mathrm{E}} f/n \\ i\, M\, \omega_{\mathrm{E}} f/n & v_{\mathrm{rel}}\, \mathfrak{S}(01001) \end{pmatrix}. \quad (6.7)$$

The $L=1$, $l=1$ element of the inverse matrix is found to be

$$\{\tilde{R}_{\mathrm{d}}^{-1*}(01)\}_M^{11} = - v_{\mathrm{rel}}^{-1} [\mathfrak{S}(01000)\, \mathfrak{S}(01001)]^{-\frac{1}{2}} \cdot \frac{i\, M\, \chi_{01}}{1 + M^2 \chi_{01}^2}\,, \quad M = 0, \pm 1\,, \quad (6.8)$$

where the effective precession angle χ_{01} has been introduced by

$$\chi_{01} = \omega_{\mathrm{E}} f/n\, v_{\mathrm{rel}} (\mathfrak{S}(01000)\, \mathfrak{S}\, 01001))^{\frac{1}{2}}\,. \quad (6.9)$$

The spherical components of the thermoelectric vector polarization can be obtained from Eq. (2.14) as

$$\langle \Phi(\boldsymbol{J})_M^1 \rangle = - \frac{1}{P} \left(\frac{m}{k_{\mathrm{B}} T} \right)^{\frac{1}{2}} \cdot \frac{\sqrt{2/5}\, \lambda_{\mathrm{trans}}\, \overline{\mathfrak{S}}\binom{01001}{10100} + \sqrt{k_{\mathrm{B}}/c_{\mathrm{rot}}}\, \lambda_{\mathrm{rot}}\, \overline{\mathfrak{S}}\binom{01001}{10010}}{(\mathfrak{S}(01000)\, \mathfrak{S}(01001))^{\frac{1}{2}}} \cdot \frac{i\, M\, \chi_{01}}{1 + M^2 \chi_{01}^2} \nabla_M T\,, \quad M = 0, \pm 1\,. \quad (6.10)$$

In Eq. (6.10), the cross sections $\overline{\mathfrak{S}}\binom{01001}{10100}$ and $\overline{\mathfrak{S}}\binom{01001}{10010}$ give rise to the Onsager-Casimir symmetry, i.e. the coupling cross sections of $\boldsymbol{J} J_{\|}$ with the heat flux represent the non-selfadjoint part of the collision operator. Switching back to Cartesian indices one obtaines (with $\boldsymbol{E}$ pointing in z-direction)

$$\langle \boldsymbol{\Phi}(\boldsymbol{J})_z \rangle = 0\,,$$
$$\langle \boldsymbol{\Phi}(\boldsymbol{J})_x \rangle \propto \nabla_y T\,, \quad \langle \boldsymbol{\Phi}(\boldsymbol{J})_y \rangle \propto \nabla_y T\,.$$

With $\boldsymbol{E} = E\boldsymbol{e}$ and $\boldsymbol{J} = \sqrt{3^{-1}}\, \langle J^2 \rangle_0^{\frac{1}{2}}\, \boldsymbol{\Phi}(\boldsymbol{J})$ the Cartesian form of the thermoelectric vector polarization is

$$\langle \boldsymbol{J} \rangle = - \frac{1}{P} \left(\frac{m\, \langle J^2 \rangle_0}{3 k_{\mathrm{B}} T} \right)^{\frac{1}{2}} \cdot \frac{\sqrt{2/5}\, \lambda_{\mathrm{trans}}\, \overline{\mathfrak{S}}\binom{01001}{10100} + \sqrt{k_{\mathrm{B}}/c_{\mathrm{rot}}}\, \lambda_{\mathrm{rot}}\, \overline{\mathfrak{S}}\binom{01001}{10010}}{(\mathfrak{S}(01000)\, \mathfrak{S}(01001))^{\frac{1}{2}}} \cdot \frac{\chi_{01}}{1 + \chi_{01}^2}\, \boldsymbol{e} \times \boldsymbol{\nabla} T\,. \quad (6.11)$$

A similar result was obtained by Hamer and Knaap [23] by use of the moment method. It should be stressed that all cross sections occurring in Eq. (6.11) vanish for a spherical interaction potential.

For an experimental investigation of the effect a plane capacitor with electric field in z-direction could be used; two insulating side walls being held at different temperatures ($\boldsymbol{\nabla} T$ in x-direction). Then a transverse vector polarization would result giving rise to a pressure independent magnetization in y-direction with a maximum value occurring at $\chi_{01}(E) = 1$.

Finally one should realize that the upper branch of the diagram involves the product of two non-diagonal Waldmann-Snider cross sections. Therefore its contribution can be neglected.

2. *Thermoelectric Tensor Polarization* $\boldsymbol{\Lambda}^{21}$

As the last example, the tensor polarization in a heat conducting gas of polar molecules under the influence of a homogeneous electric field is studied. The corresponding diagram is

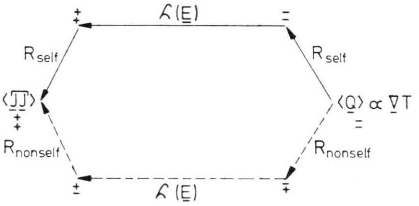

Fig. 4. Schematic diagram for the possible branches which lead to a $\overline{\boldsymbol{J}\boldsymbol{J}}$-polarization in a heat flow.

While one branch involves twice the selfadjoint part of the collision operator, in the other the non-selfadjoint part occurs twice. The situation is therefore very similar to the Senftleben-Beenakker effect [4]. The terms connected with R_{nonself} are known to account only for a few percents of the total effect. Thus effects quadratic in R_{nonself} are disregarded here.

For the upper branch the simplest choice of expansion tensors consists in taking $p=1$, $q=2$, $\alpha=0$ (Kagan polarization) and $\alpha' = \{100\}, \{001\}$. The resulting polarization production coefficient is

$$\Lambda_M^{21} = \frac{v_{\mathrm{rel}}}{3} \sum_{\alpha'} \{\tilde{R}_{\mathrm{d}}^{-1*}(1,2)\}_M^{21}\, \overline{\mathfrak{S}}\binom{12000}{10\alpha'}_1 \cdot \langle\langle \boldsymbol{\Phi}^{10\alpha'} | \cdot R_{\mathrm{d}}^{-1} \boldsymbol{Q} \rangle\rangle\,. \quad (6.12)$$

To evaluate the matrix element of $\tilde{R}_{\mathrm{d}}^{-1*}(1,2)$, one needs the following set of expansion tensors:

$[\boldsymbol{\Phi}^{12000}]^{1,2,3}$, $[\boldsymbol{\Phi}^{12001}]^{1,2,3}$, $\boldsymbol{\Phi}^{02000}$, $\boldsymbol{\Phi}^{02001}$. The relevant matrix elements of the Liouville operator are

$$\langle\langle \Phi^{12001}_{MN} \,|\, \mathscr{L}(\boldsymbol{E})\, \Phi^{12000}_{M'N'} \rangle\rangle = -\, N'\, \omega_{\mathrm{E}} \frac{f'}{n}\, \delta_{MM'}\, \delta_{NN'} \,,$$

$$\langle\langle \Phi^{02001}_{M} \,|\, \mathscr{L}(\boldsymbol{E})\, \Phi^{02000}_{M'} \rangle\rangle = -\, M'\, \omega_{\mathrm{E}} \frac{f'}{n}\, \delta_{MM'} \,, \tag{6.13}$$

with

$$f' = \langle (J^2 - \tfrac{3}{4})\, J_{\parallel}{}^2 \rangle_0 / (\langle J^2 (J^2 - \tfrac{3}{4})\, J_{\parallel}{}^2 \rangle_0 \, \langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0)^{\frac{1}{2}} \,. \tag{6.14}$$

The pertaining matrix $\{\tilde{R}^{*}_{\mathrm{d}}(12)\}_M$ is: (6.15)

$$\{\tilde{R}^{*}_{\mathrm{d}}(12)\}_M \triangleq \begin{pmatrix}
v_{\mathrm{rel}}\, \overline{\mathfrak{S}}(12000)_1 & 0 & 0 & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{11}_M & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{12}_M & 0 & 0 & 0 \\
0 & v_{\mathrm{rel}}\, \overline{\mathfrak{S}}(12000)_2 & 0 & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{12}_M & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{22}_M & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{23}_M & 0 & -\,i\, v_{\mathrm{rel}}\, \overline{\mathfrak{S}}\binom{02001}{12000} \\
0 & 0 & v_{\mathrm{rel}}\, \overline{\mathfrak{S}}(12000)_3 & 0 & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{23}_M & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{33}_M & 0 & 0 \\
i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{11}_M & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{12}_M & 0 & v_{\mathrm{rel}}\, \overline{\mathfrak{S}}(12001)_1 & 0 & 0 & 0 & 0 \\
i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{12}_M & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{22}_M & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{23}_M & 0 & v_{\mathrm{rel}}\, \overline{\mathfrak{S}}(12001)_2 & 0 & -\,i\, v_{\mathrm{rel}}\, \overline{\mathfrak{S}}\binom{12001}{02000} & 0 \\
0 & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{23}_M & i\,\omega_{\mathrm{E}} \frac{f'}{n} F^{33}_M & 0 & 0 & v_{\mathrm{rel}}\, \overline{\mathfrak{S}}(12001)_3 & 0 & 0 \\
\boxed{0} & 0 & 0 & 0 & i\, v_{\mathrm{rel}}\, \overline{\mathfrak{S}}\binom{12001}{02000} & 0 & v_{\mathrm{rel}}\, \mathfrak{S}(02000) & i\, M\, \omega_{\mathrm{E}} \frac{f'}{n} \\
0 & i\, v_{\mathrm{rel}}\, \overline{\mathfrak{S}}\binom{02001}{12000} & 0 & 0 & 0 & 0 & i\, M\, \omega_{\mathrm{E}} \frac{f'}{n} & v_{\mathrm{rel}}\, \mathfrak{S}(02001)
\end{pmatrix}$$

In Eq. (6.15), $F^{ll'}_M = F^{ll'}_M(12)$ of Eq. (5.10) has to be inserted. For the calculation of the relevant element of the inverse matrix the spherical approximation will be made, i.e. $\overline{\mathfrak{S}}(12000)_L = \mathfrak{S}(12000)$, $\overline{\mathfrak{S}}(12001)_L = \mathfrak{S}(12001)$ for $L = 1, 2, 3$ and terms quadratic in nondiagonal collision cross sections are neglected. The desired element of the inverse matrix is then found to be

$$\{\tilde{R}_{\mathrm{d}}^{-1*}(12)\}^{21}_M = \tfrac{1}{2} \sqrt{3/5}\, \sqrt{4 - M^2}\, [v_{\mathrm{rel}} (1 + M^2 \chi^2_{02}) (1 + \chi^2_{12} (2 + 3 M^2) + \chi^4_{12} (1 + 3 M^4) + \chi^6_{12} M^2 (1 - M^2)^2]^{-1}$$
$$\cdot \left(\frac{-\, \overline{\mathfrak{S}}\binom{02000}{12001} \chi_{12} (1 + (1 - M^2)\, \chi^2_{12} + \tfrac{2}{3} \chi^4_{12} M^2 (1 - M^2))}{\mathfrak{S}(02000)\, (\mathfrak{S}(12000)\, \mathfrak{S}(12001))^{\frac{1}{2}}} + \frac{\overline{\mathfrak{S}}\binom{02001}{12000} M^2 \chi_{02}\, \chi^2_{12} (7 + \chi^2_{12} (1 + 3 M^2))}{3\, \mathfrak{S}(12000)\, (\mathfrak{S}(02000)\, \mathfrak{S}(02001))^{\frac{1}{2}}} \right). \tag{6.16}$$

The precession angles χ_{02}, χ_{12} are given by

$$\chi_{02} = \omega_E f'/n\, v_{\mathrm{rel}} (\mathfrak{S}(02000)\, \mathfrak{S}(02001))^{\frac{1}{2}}, \qquad \chi_{12} = \omega_E f'/n\, v_{\mathrm{rel}} (\mathfrak{S}(12000)\, \mathfrak{S}(12001))^{\frac{1}{2}}. \tag{6.17}$$

The matrix element Eq. (6.16) vanishes for $M = \pm 2$ as is to be expected. The terms with $M^2(1-M^2)$ can be omitted since they are zero for $M = 0, \pm 1$. From Eqs. (6.12), (6.16), (6.3), (6.4) the spherical components of the thermoelectric tensor polarization are found to be

$$\langle J_0{}^2 \rangle = A_0 \nabla_0 T, \quad \langle J^2_{\pm 1} \rangle = A_1 \nabla_{\pm 1} T, \tag{6.18}$$

$$\begin{aligned} A_0 = &- \frac{1}{5P} (2m\, k_B^{-1}\, T^{-1} \langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0)^{\frac{1}{2}} \left(\sqrt{2/5}\, \lambda_{\mathrm{transl}}\, \overline{\mathfrak{S}}\tbinom{12000}{10100} + \sqrt{k_B/c_{\mathrm{rot}}}\, \lambda_{\mathrm{rot}}\, \overline{\mathfrak{S}}\tbinom{12000}{10010}\right) \\ &\cdot \frac{\overline{\mathfrak{S}}\binom{02000}{12001}}{\mathfrak{S}(02000)\, (\mathfrak{S}(12000)\, \mathfrak{S}(12001))^{\frac{1}{2}}} \frac{\chi_{12}}{1+\chi_{12}^2}, \end{aligned} \tag{6.19}$$

$$\begin{aligned} A_1 = &+ \frac{1}{5P} (\tfrac{1}{6} m\, k_B^{-1}\, T^{-1} \langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0)^{\frac{1}{2}} \left(\sqrt{2/5}\, \lambda_{\mathrm{transl}}\, \overline{\mathfrak{S}}\tbinom{12000}{10100} + \sqrt{k_B/c_{\mathrm{rot}}}\, \lambda_{\mathrm{rot}}\, \overline{\mathfrak{S}}\tbinom{12000}{10010}\right) \frac{1}{1+\chi_{02}^2} \\ &\cdot \left\{ \frac{-\overline{\mathfrak{S}}\binom{02000}{12001}}{\mathfrak{S}(02000)\, (\mathfrak{S}(12000)\, \mathfrak{S}(12001))^{\frac{1}{2}}} \left(\frac{\chi_{12}}{1+\chi_{12}^2} - 2 \frac{2\chi_{12}}{1+4\chi_{12}^2} \right) \right. \\ &\left. + \frac{\overline{\mathfrak{S}}\binom{02001}{12000}}{\mathfrak{S}(12000)\, (\mathfrak{S}(02000)\, \mathfrak{S}(02001))^{\frac{1}{2}}} \chi_{02} \left(\frac{\chi_{12}^2}{1+\chi_{12}^2} - \frac{8\chi_{12}^2}{1+4\chi_{12}^2} \right) \right\}. \end{aligned} \tag{6.20}$$

The relaxation cross sections $\mathfrak{S}(12000)$, $\mathfrak{S}(12001)$, and the coupling cross sections $\overline{\mathfrak{S}}\binom{12000}{10100}$, $\overline{\mathfrak{S}}\binom{12000}{10010}$ can be inferred from the Senftleben-Beenakker effects on heat conductivity [24, 25], while the relaxation cross sections $\mathfrak{S}(02000)$ and $\mathfrak{S}(02001)$ can be taken from the Senftleben-Beenakker effects on viscosity [24, 26]. Thus the unknown cross sections occurring in Eqs. (6.19), (6.20) are $\overline{\mathfrak{S}}\binom{02000}{12001}$ and $\overline{\mathfrak{S}}\binom{02001}{12000}$.

Switching from the spherical tensor notation to the Cartesian tensor notation used in Eq. (1.4), $\langle \overline{\boldsymbol{J}\boldsymbol{J}} \rangle = \alpha_1 \overline{\boldsymbol{e} \boldsymbol{\nabla} T} + \alpha_2\, \boldsymbol{e} \cdot \boldsymbol{\nabla} T\, \overline{\boldsymbol{e}\boldsymbol{e}}$ and observing the interrelation

$$\alpha_1 = \sqrt{2}\, A_1, \quad \alpha_2 = \sqrt{3/2}\, A_0 - \sqrt{2}\, A_1 \tag{6.21}$$

one obtains

$$\begin{aligned} \langle \overline{\boldsymbol{J}\boldsymbol{J}} \rangle = &- \frac{1}{5P} (3m\, k_B^{-1}\, T^{-1} \langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0)^{\frac{1}{2}} \left(\sqrt{2/5}\, \lambda_{\mathrm{transl}}\, \overline{\mathfrak{S}}\tbinom{12000}{10100} + \sqrt{k_B/c_{\mathrm{rot}}}\, \lambda_{\mathrm{rot}}\, \overline{\mathfrak{S}}\tbinom{12000}{10010}\right) \\ &\cdot \left\{ \frac{1}{1+\chi_{02}^2} \left(\frac{\overline{\mathfrak{S}}\binom{02000}{12001}}{\mathfrak{S}(02000)\, (\mathfrak{S}(12000)\, \mathfrak{S}(12001))^{\frac{1}{2}}} \frac{\chi_{12}}{(1+\chi_{12}^2)(1+4\chi_{12}^2)} \right. \right. \\ &\left. - \frac{\overline{\mathfrak{S}}\binom{02001}{12000}}{3\, \mathfrak{S}(12000)\, (\mathfrak{S}(02000)\, \mathfrak{S}(02001))^{\frac{1}{2}}} \chi_{02} \left(\frac{8\chi_{12}^2}{1+4\chi_{12}^2} - \frac{\chi_{12}^2}{1+\chi_{12}^2} \right) \right) \overline{\boldsymbol{e} \boldsymbol{\nabla} T} \\ &+ \left(\frac{\overline{\mathfrak{S}}\binom{02000}{12001}}{\mathfrak{S}(02000)\, (\mathfrak{S}(12000)\, \mathfrak{S}(12001))^{\frac{1}{2}}} \frac{\chi_{12}}{1+\chi_{12}^2} \left(1 - \frac{1}{(1+\chi_{02}^2)(1+4\chi_{12}^2)} \right) \right. \\ &\left. \left. + \frac{\overline{\mathfrak{S}}\binom{02001}{12000}}{3\, \mathfrak{S}(12000)\, (\mathfrak{S}(02000)\, \mathfrak{S}(02001))^{\frac{1}{2}}} \frac{\chi_{02}}{1+\chi_{02}^2} \left(\frac{8\chi_{12}^2}{1+4\chi_{12}^2} - \frac{\chi_{12}^2}{1+\chi_{12}^2} \right) \right) \boldsymbol{e} \cdot \boldsymbol{\nabla} T\, \overline{\boldsymbol{e}\boldsymbol{e}} \right\}. \end{aligned} \tag{6.22}$$

It is seen that the alignment goes through a maximum as a function of the electric field strength E. Since the friction pressure tensor is connected with $\langle \overline{\boldsymbol{J}\boldsymbol{J}} \rangle$ it follows that in a heat conducting gas a friction pressure exists which has a contribution linear in the temperature gradient. The occurrence of such a visco-thermal cross effect (which is a Burnett effect) has already been stated in Ref. [18].

If heat flow birefringence proportional to $\boldsymbol{\nabla} T$ is considered, $\langle \overline{\boldsymbol{J}\boldsymbol{J}} \rangle$ has to be replaced by

$$\langle \overline{\boldsymbol{J}\boldsymbol{J}} / (J^2 - \tfrac{3}{4}) \rangle;$$

accordingly $\langle J^2 (J^2 - \frac{3}{4}) \rangle_0$ has to be replaced by $\langle J^2 / (J^2 - \frac{3}{4}) \rangle_0$. For an experiment with electric field in z-direction and temperature gradient in x-direction, the major axes of the dielectric tensor are $\boldsymbol{e}_y$ (unit vector in y-direction which should be chosen as the axis of light propagation) and $1/\sqrt{2}\,(\boldsymbol{e}_x \pm \boldsymbol{e}_z)$. The situation is thus quite similar to flow birefringence [3].

Finally it should be stressed that, while the polarizations are always inversely proportional to the pressure, the corresponding macroscopic observables $\boldsymbol{M}$ (magnetization) and $\overline{\boldsymbol{\epsilon}}$ (anisotropic part of the dielectric tensor) are pressure independent.

VII. An "alternative" derivation of $\boldsymbol{\Lambda}_M^{Ll}$

The results of the coefficients can be obtained in an somewhat more straightforward method by using a splitting procedure for R that is different from the one introduced in Eq. (4.1). One again writes

$$R = R_{\mathrm{d}} \oplus R_{\mathrm{nd}} \tag{7.1}$$

but now R_{d} couples within space S_1 and within the subspaces S_{2i} $(i = L \ldots)$ in which S_2 is divided. R_{nd} couples between S_1 and the subspaces and also between different subspaces

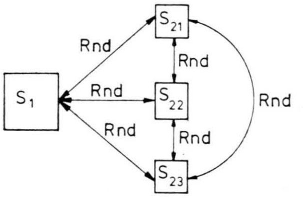

Fig. 5. The coupling between the various subspaces through R_{nd}.

In this procedure the subspaces of S_2 are chosen such that they contain one of the various polarizations $\boldsymbol{W}^p \boldsymbol{J}^q$ with $q \neq 0$. The rationalization for this procedure is that the matrix elements that couple the various angular momentum polarizations are small.

Much of what has been done in Sect. VI remains valid although R_{d} and R_{nd} have now a slightly different meaning (see Eqs. (4.2) and (4.3)).

We now get for instead of Eq. (5.1)

$$\Lambda_{Mm}^{22} = +\sqrt{2}\,\langle\langle \Phi_M^{02} | \tilde{R}_{\mathrm{d}}^{-1}\, \Phi_m^{20} \rangle\rangle^* , \tag{7.2}$$

$$\Lambda_{Mm}^{22} = -\sqrt{2} \sum_{\alpha,\beta} \langle\langle \Phi_M^{02} | \tilde{R}_{\mathrm{d}}^{-1}\, \Phi_\alpha^{02} \rangle\rangle^* \cdot \langle\langle \Phi_\alpha^{02} | R_{\mathrm{nd}}\, \Phi_\beta^{20} \rangle\rangle^* \langle\langle \Phi_\beta^{20} | R_{\mathrm{d}}^{-1}\, \Phi_m^{20} \rangle\rangle , \tag{7.3}$$

$$\Lambda_M^{22} = -\sqrt{2}\,(1 + i\,M\,\varphi_{02})^{-1} \frac{\mathfrak{S}\binom{02}{20}}{\mathfrak{S}(02)} \frac{\eta}{k_{\mathrm{B}}\,T} \tag{7.4}$$

which is the equivalent to Equation (5.3). In fact in this case the methods do not differ.

For the viscomagnetic vector polarization $\boldsymbol{\Lambda}^{12}$ one gets

$$\begin{aligned} \Lambda_{Mm}^{12} &= \sqrt{2}\,\langle\langle \Phi_M^{01} | \tilde{R}_{\mathrm{d}}^{-1}\, \Phi_m^{20} \rangle\rangle^* \\ &= \sqrt{2} \sum_{\alpha,\beta,\gamma,\delta,\varepsilon,\zeta} \langle\langle \Phi_M^{01} | \tilde{R}_{\mathrm{d}}^{-1}\, \Phi_\alpha^{01} \rangle\rangle^* \\ &\quad \cdot \langle\langle \Phi_\alpha^{01} | R_{\mathrm{nd}}\, \Phi_{\beta\gamma}^{21} \rangle\rangle^* \langle\langle \Phi_{\beta\gamma}^{21} | \tilde{R}_{\mathrm{d}}^{-1}\, \Phi_{\delta\varepsilon}^{21} \rangle\rangle^* \\ &\quad \cdot \langle\langle \Phi_{\delta\varepsilon}^{21} | R_{\mathrm{nd}}\, \Phi_\zeta^{20} \rangle\rangle^* \ll \Phi_\zeta^{20} | \tilde{R}_{\mathrm{d}}^{-1}\, \Phi_m^{20} \gg . \end{aligned} \tag{7.5}$$

In deriving Eq. (7.5) we expanded $\tilde{R}_{\mathrm{d}}^{-1}$ up to second order in R_{nd}.

The result appears now as a product of 5 terms, the advantage being that one avoids the matrix inversion of in this case the 4-by-4 matrix of Eq. (5.8) (later of an 8-by-8 matrix). Furthermore one does not need the expressions F_M^{Ll} involved in Eqs. (5.8) and (6.15).

Using the expressions (7.13) to reduce the various brackets one gets

$$\Lambda_{Mm}^{12} = -i \sum_{\beta\gamma} \frac{5\sqrt{3} \begin{pmatrix} 1 & 2 & 1 \\ -M & \beta & \gamma \end{pmatrix} \begin{pmatrix} 2 & 1 & 2 \\ -\beta & -\gamma & m \end{pmatrix}}{\{1 + i\,M\,\varphi_{01}\}\{1 + i\,\gamma\,\varphi_{21}\}} \cdot \frac{\mathfrak{S}\binom{01}{21}\,\mathfrak{S}\binom{21}{20}}{v_{\mathrm{rel}}\,\mathfrak{S}(01)\,\mathfrak{S}(21)\,\mathfrak{S}(20)} . \tag{7.6}$$

This equation is seen to be equivalent to Eqs. (5.12) and (5.13), if one uses the expression (see Eq. (7.16) or (7.17))

$$\mathfrak{S}\binom{01}{21}\,\mathfrak{S}\binom{21}{20} = \sqrt{2/5}\;\overline{\mathfrak{S}}\binom{01}{21}\,\overline{\mathfrak{S}}\binom{21}{20} , \tag{7.7}$$

all other symbols having the same meaning. The connection between $\mathfrak{S}\binom{p\,q}{p'q'}$ and $\overline{\mathfrak{S}}\binom{pq}{p'q'}$ is discussed at the end of this section.

For Λ_{Mm}^{11} one gets

$$\begin{aligned} \Lambda_{Mm}^{11} &= \langle\langle \Phi_M^{01} | \tilde{R}_{\mathrm{d}}^{-1}\, Q_m \rangle\rangle^* \\ &= -\sum_{\alpha,\beta} \langle\langle \Phi_M^{01000} | \tilde{R}_{\mathrm{d}}^{-1}\, \Phi_\alpha^{01001} \rangle\rangle^* \\ &\quad \cdot \left\{ \begin{aligned} &\langle\langle \Phi_\alpha^{01001} | R_{\mathrm{nd}}\, \Phi_\beta^{10100} \rangle\rangle \langle\langle \Phi_\beta^{10100} | R_{\mathrm{d}}^{-1}\, Q_m^1 \rangle\rangle \\ +\, &\langle\langle \Phi_\alpha^{01001} | R_{\mathrm{nd}}\, \Phi_\beta^{10010} \rangle\rangle \langle\langle \Phi_\beta^{10010} | R_{\mathrm{d}}^{-1}\, Q_m^1 \rangle\rangle \end{aligned} \right\} . \end{aligned} \tag{7.8}$$

Only terms up to the first order in R_{nd} are needed in this case. Using the fact that the matrix involved in the inversion of the first therm can be written as

$$\begin{pmatrix} v_{\mathrm{rel}}\,\mathfrak{S}(01000) & -i\,M\,\omega_{\mathrm{E}}\,f\,M/n \\ -i\,M\,\omega_{\mathrm{E}}\,f\,M/n & v_{\mathrm{rel}}\,\mathfrak{S}(01001) \end{pmatrix}$$

one finds

$$\begin{aligned} \Lambda_{Mm}^{11} = i\,&\frac{M\,\chi_{01}}{1 + M^2\,\chi_{01}^2} (\mathfrak{S}(01000)\,\mathfrak{S}(01001))^{-\frac{1}{2}} \\ &\cdot \left(\frac{m}{k_{\mathrm{B}}\,T}\right)^{\frac{1}{2}} \frac{1}{k_{\mathrm{B}}} \{\sqrt{2/5}\,\lambda_{\mathrm{transl}}\,\mathfrak{S}\tbinom{01001}{10100} \\ &+ \sqrt{k_{\mathrm{B}}/c_{\mathrm{rot}}}\,\lambda_{\mathrm{rot}}\,\mathfrak{S}\tbinom{01001}{10010}\}\,\delta_{Mm} . \end{aligned} \tag{7.9}$$

This result is seen to be equivalent to the results of Eqs. (6.10) and (6.11).

The last coefficient $\mathbf{\Lambda}^{21}$ requires expansion to second order in R_{nd}.

$$\begin{aligned} \Lambda^{21}_{Mm} &= \langle\langle \Phi^{02}_{M} | \tilde{R}_{\mathrm{d}}^{-1} Q^{1}_{m} \rangle\rangle^* = \sum_{\alpha,\beta,\gamma,\delta,\varepsilon,\zeta} \\ &\cdot \left\{ \begin{array}{l} \langle\langle \Phi^{02000}_{M} | \tilde{R}_{\mathrm{d}}^{-1} \Phi^{02000}_{\alpha} \rangle\rangle^* \langle\langle \Phi^{02}_{\alpha} | R_{\mathrm{nd}} \Phi^{12001}_{\beta\gamma} \rangle\rangle^* \langle\langle \Phi^{12001}_{\beta\gamma} | \tilde{R}_{\mathrm{d}}^{-1} \Phi^{12000}_{\delta\varepsilon} \rangle\rangle^* \\ + \langle\langle \Phi^{02000}_{M} | \tilde{R}_{\mathrm{d}}^{-1} \Phi^{02001}_{\alpha} \rangle\rangle^* \langle\langle \Phi^{02001}_{\alpha} | R_{\mathrm{nd}} \Phi^{12000}_{\beta\gamma} \rangle\rangle^* \langle\langle \Phi^{12000}_{\beta\gamma} | \tilde{R}_{\mathrm{d}}^{-1} \Phi^{12000}_{\delta\varepsilon} \rangle\rangle^* \end{array} \right\} \\ &\cdot \left\{ \begin{array}{l} \langle\langle \Phi^{12000}_{\delta\varepsilon} | R_{\mathrm{nd}} \Phi^{10100}_{\zeta} \rangle\rangle^* \langle\langle \Phi^{10100}_{\zeta} | R_{\mathrm{d}}^{-1} Q^{1}_{m} \rangle\rangle \\ + \langle\langle \Phi^{12000}_{\delta\varepsilon} | R_{\mathrm{nd}} \Phi^{10010}_{\zeta} \rangle\rangle^* \langle\langle \Phi^{10010}_{\zeta} | R_{\mathrm{d}}^{-1} Q^{1}_{m} \rangle\rangle \end{array} \right\}, \end{aligned} \tag{7.10}$$

$$\begin{aligned} \Lambda^{21}_{Mm} = &- \frac{5\sqrt{3/2}}{P} \frac{1}{T} \sqrt{\frac{m}{k_{\mathrm{B}} T}} \sum_{\beta,\gamma} \begin{pmatrix} 2 & 1 & 2 \\ -M & \beta & \gamma \end{pmatrix} \begin{pmatrix} 1 & 2 & 1 \\ -\beta & -\gamma & m \end{pmatrix} \{(1 + M^2 \chi_{02}^2)(1 + \gamma^2 \chi_{12}^2)\}^{-1} \\ &\cdot \left\{ \frac{\gamma \chi_{12}\, \mathfrak{S}\binom{02000}{12001}}{\mathfrak{S}(02000)\, (\mathfrak{S}(12000)\, \mathfrak{S}(12001))^{\frac{1}{2}}} + \frac{M \chi_{02}\, \mathfrak{S}\binom{02001}{12000}}{\mathfrak{S}(12000)\, (\mathfrak{S}(02000)\, \mathfrak{S}(02001))^{\frac{1}{2}}} \right\} \\ &\cdot \left\{ \sqrt{2/5}\, \lambda_{\mathrm{transl}}\, \mathfrak{S}\binom{12000}{10100} + \sqrt{k_{\mathrm{B}}/c_{\mathrm{rot}}}\, \lambda_{\mathrm{rot}}\, \mathfrak{S}\binom{12000}{10010} \right\}. \end{aligned} \tag{7.11}$$

This is found to be equivalent to Eqs. (6.10) and (6.20) if one uses (see Eqs. (7.17) or (7.16))

$$\mathfrak{S}\binom{02000}{12001} \mathfrak{S}\binom{12000}{10100} = \sqrt{2/5}\, \overline{\mathfrak{S}}\binom{02000}{12001} \overline{\mathfrak{S}}\binom{12000}{10100} \quad \text{and} \quad \mathfrak{S}\binom{02001}{12000} \mathfrak{S}\binom{12000}{10100} = \sqrt{2/5}\, \overline{\mathfrak{S}}\binom{02001}{12000} \overline{\mathfrak{S}}\binom{12000}{10100}. \tag{7.12}$$

In Eqs. (7.4), (7.6), (7.9), and (7.11) use is made of a relation between a scalar cross section and a spherical component of a tensorial matrix element of the collision superoperator. This expression is in the coupling scheme of Chen, Moraal and Snider (see Eq. (20b) of Ref. [20])*.

$$\begin{aligned} \langle\langle \Phi^{pqrst}_{\mu\nu} | R\, \Phi^{p'q'r's't'}_{\mu'\nu'} \rangle\rangle &= v_{\mathrm{rel}}\, i^{p-p'+q-q'} \sum_{k\varkappa} (-1)^{k+p+q+\mu+\nu'} \Omega(k\, q'\, q)^{\frac{1}{2}} \\ &\cdot \Omega(k\, p'\, p)^{\frac{1}{2}} \begin{pmatrix} k & q & q' \\ \varkappa & -\nu & \nu' \end{pmatrix} \begin{pmatrix} k & p & p' \\ -\varkappa & -\mu & \mu' \end{pmatrix} \mathfrak{S}_k \begin{pmatrix} p & q & r & s & t \\ p' & q' & r' & s' & t' \end{pmatrix}, \end{aligned} \tag{7.13}$$

where

$$\Omega(k\, p'\, p) = \frac{(p + p' + k + 1)!\, (p + p' - k)!\, (p - p' + k)!\, (p' - p + k)!}{(2k)!\, (2p)!\, (2p')!} \, \frac{3 - (-1)^{p+p'+k}}{2}.$$

When only one value for k is possible in Eq. (7.13) the subscript of $\mathfrak{S}_k$ is often dropped. Using time reversal one finds for the scalar cross sections

$$\mathfrak{S}_k \begin{pmatrix} p & q & r & s & t \\ p' & q' & r' & s' & t' \end{pmatrix} = (-1)^{t-t'}\, \mathfrak{S}_k \begin{pmatrix} p' & q' & r' & s' & t' \\ p & q & r & s & t \end{pmatrix}. \tag{7.14}$$

The cross sections $\overline{\mathfrak{S}}_L$ used in Sects. 4, 5 and 6 are defined in Eq. (4.5). The coupling scheme is outlined by the definition of $[\Phi^{pq}]^L_M$ as stated in Eq. (2.17). For these scalar cross sections one obtains

$$\overline{\mathfrak{S}} \begin{pmatrix} p & q & r & s & t \\ p' & q' & r' & s' & t' \end{pmatrix}_L = (-1)^{p-p'+q-q'+t-t'}\, \overline{\mathfrak{S}} \begin{pmatrix} p' & q' & r' & s' & t' \\ p & q & r & s & t \end{pmatrix}_L \tag{7.15}$$

which differs from Eq. (7.14).

The two types of cross sections are related to each other by

$$\overline{\mathfrak{S}} \begin{pmatrix} p & q & r & s & t \\ p' & q' & r' & s' & t' \end{pmatrix}_L = \sum_k \Omega(k\, q'\, q)^{\frac{1}{2}}\, \Omega(k\, p'\, p)^{\frac{1}{2}} (-1)^{k+p+q'+L} \begin{Bmatrix} q & p & L \\ p' & q' & k \end{Bmatrix} \mathfrak{S}_k \begin{pmatrix} p & q & r & s & t \\ p' & q' & r' & s' & t' \end{pmatrix} \tag{7.16}$$

and

$$\mathfrak{S}_k \begin{pmatrix} p & q & r & s & t \\ p' & q' & r' & s' & t' \end{pmatrix} = \sum_L \frac{(2L+1)(2k+1)}{\Omega(k\, q'\, q)^{\frac{1}{2}}\, \Omega(k\, p'\, p)^{\frac{1}{2}}} (-1)^{k+p+q'+L} \begin{Bmatrix} q & p & L \\ p' & q' & k \end{Bmatrix} \overline{\mathfrak{S}} \begin{pmatrix} p & q & r & s & t \\ p' & q' & r' & s' & t' \end{pmatrix}_L. \tag{7.17}$$

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* It must be remembered that in this paper the spherical Edmonds' basis [16] is used (see Eq. (5.14)).

With the help of these equations the relations between the cross sections in Eqs. (7.7) and (7.12) have been derived. The cross sections

$$\mathfrak{S}\begin{pmatrix} p & q & r & s & t \\ p' & q' & r' & s' & t' \end{pmatrix}^{(\alpha)}$$

also used in Ref. [20], are obtained with an analogous coupling scheme as the $\overline{\mathfrak{S}}_L$; but their $[\Phi^{pq}]^L_M$ differ slightly from those of Eq. (2.17) [27]. This means that those cross sections have the same time reversal property as $\overline{\mathfrak{S}}_L$ (Eq. (7.15)), but differ by a phase factor:

$$\overline{\mathfrak{S}}\begin{pmatrix} p & q & r & s & t \\ p' & q' & r' & s' & t' \end{pmatrix}_L = (-1)^{p+p'+q+q'}\,\mathfrak{S}\begin{pmatrix} p & q & r & s & t \\ p' & q' & r' & s' & t' \end{pmatrix}^{(\alpha)}. \tag{7.18}$$

Acknowledgements

The authors are indebted to Dr. D. A. Coombe for clarifying the differences between the various cross sections and also thank Dr. H. Vestner and Dr. J. Halbritter for stimulating discussions.

One of the authors (H.F.P. K.) wishes to express his gratitude to the "Deutsche Forschungsgemeinschaft" for making possible his visit to Erlangen.

This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.)" and has been made possible by financial support from the "Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Z.W.O.)".

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