On the Nonspherical Scattering Amplitude for Inelastic Molecular Collisions

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The rotational angular momentum dependence of the nonspherical scattering amplitude is investigated for inelastic collisions of linear molecules. As far as the approximation of small nonsphericity can be applied, this dependence is obtained from the angular momentum dependence of the nonspherical interaction potential. The connection between the nonspherical scattering amplitude and observables that can be measured by molecular scattering experiments involving a polarized beam is discussed. Some qualitative remarks are made on collision brackets occurring in the theoretical expressions for the bulk viscosity and for the Senftleben-Beenakker effect for H_2 and HD.

In a previous paper [1] the dependence of the nonspherical binary scattering amplitude operator on the rotational angular momenta of the colliding particles has been studied for energetically elastic collisions of linear nonpolar molecules. This paper is concerned with the corresponding investigation for inelastic collisions, i. e., collisions which induce transitions between the rotational levels of the colliding molecules. Furthermore, the relevance of the nonspherical scattering amplitude for molecular beam scattering experiments with polarized (aligned) molecules is discussed and some consequences for collision brackets are mentioned.

The nonsphericity of the scattering amplitude is of crucial importance for a great number of transport and relaxation phenomena in dilute polyatomic gases, in particular for the relaxation of the difference between the translational and rotational temperatures [2, 3] (bulk viscosity), for the influence of magnetic and electric fields on the heat conductivity and viscosity [4, 5] (Senftleben-Beenakker effects), for flow birefringence [6] and the electric polarization caused by a temperature gradient [6a], for nuclear spin relaxation [7], for depolarized Rayleigh light scattering [8, 9], and for rotational Raman scattering [10]. Using an approach based on the quantum mechanical kinetic equation [11] the relevant relaxation and transport coefficients and spectral line-widths can be expressed in terms of collision brackets involving the binary scattering amplitude operator and its adjoint. The temperature relaxation coefficient can be reduced to a collision bracket containing the inelastic differential cross section averaged over initial and summed over final magnetic quantum numbers. A knowledge of the scattering amplitude operator (matrix with respect to the magnetic quantum numbers), however, is required for a calculation of the collision brackets associated with all the other transport and relaxation phenomena mentioned above.

The nonspherical scattering amplitude is also of interest for the interpretation of molecular beam scattering experiments with polarized (aligned) par-

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ticles [12] as well as for a comparison of measurements of transport and relaxation coefficients with data obtained from these scattering experiments.

Inelastic differential cross sections have been studied theoretically by a great number of investigators, for a survey of the literature see Ref. [13, 14]. Total cross sections for collisions of H_2 molecules in a specific rotational level and magnetic substate with monatomics have been calculated by REUSS and STOLTE [15]. Reorientation cross sections needed for NMR in gaseous H_2 have been treated by KINSEY, RIEHL and WAUGH [16].

This paper proceeds as follows: Firstly, a statement is given of the relation connecting the scattering amplitude and the scattering $\mathcal{T}$ matrix which, in turn, is related to the interaction potential by the Lippmann-Schwinger equation. Then the nonsphericity parameter ε which, in essence, measures the ratio of the nonspherical and spherical parts of the interaction potential, is introduced. Assuming that ε is small (small nonsphericity) one can expand the $\mathcal{T}$ matrix with respect to this parameter (§ 1). The dependence of the nonspherical $\mathcal{T}$ operator (and consequently of the scattering amplitude operator) in order ε on the rotational angular momenta of the colliding particles is closely connected with the rotational angular momentum dependence of the nonspherical interaction potential. Therefore some general features of the nonspherical interaction potential are studied for linear molecules where the interaction depends on the direction of the molecular axes and the line connecting the centers of mass of the colliding molecules (§ 2). Next, a transcription of these "angle dependent" interaction potentials into a "spin operator" form is given. The "spin operators" are (spherical or Cartesian) tensor operators which exhibit the dependence on the rotational angular momenta. Thus it is possible to obtain the rotational angular momentum dependence of the scattering amplitude in order ε in a rather simple way. As specific examples, the hydrogen molecules H_2 and HD are considered (§ 3). Observables that can be measured in a molecular scattering experiment with a polarized beam and their relation to the nonspherical scattering amplitude are discussed in § 4. Finally, some order of magnitude considerations are given for collision brackets that occur in connection with the temperature relaxation (bulk viscosity) and the Senftleben-Beenakker effect of the viscosity and the heat conductivity of H_2 and HD (§ 5).

§ 1. Scattering Amplitude in the Approximation of Small Nonsphericity

The scattering amplitude operator $a(\boldsymbol{k}, \boldsymbol{k}')$ is linked with the binary scattering $\mathcal{T}$ operator in the center of mass system by

$$a(\boldsymbol{k}, \boldsymbol{k}') = -\frac{m_{12}}{2\pi\hbar^2} \langle \boldsymbol{k} | \mathcal{T} | \boldsymbol{k}' \rangle , \qquad (1.1)$$

where, in the x-representation, $\langle \boldsymbol{x} | \boldsymbol{k} \rangle = \exp\{i k \boldsymbol{e} \cdot \boldsymbol{x}\}$ and $\langle \boldsymbol{x} | \boldsymbol{k}' \rangle = \exp\{i k' \boldsymbol{e}' \cdot \boldsymbol{x}\}$ are plane waves with $\boldsymbol{e}$ and $\boldsymbol{e}'$ being unit vectors in the directions of the relative linear momenta $\hbar \boldsymbol{k}$ and $\hbar \boldsymbol{k}'$ after and before the collision, $\boldsymbol{x} = r \hat{\boldsymbol{x}}$ is the relative position vector of the centers of mass of the colliding particles and m_{12} is their reduced mass.

The scattering $\mathcal{T}$ operator is related to the interaction potential by the Lippman-Schwinger equation

$$\mathcal{T} = \mathcal{V} + \mathcal{V} G_0^{(+)} \mathcal{T} , \qquad (1.2)$$

and the "formal solution" of (1.2) is

$$\mathcal{T} = \mathcal{V} + \mathcal{V} \mathcal{G}^{(+)} \mathcal{V} , \qquad (1.3)$$

where $\mathcal{G}^{(+)} = (E - H + i\eta)^{-1}$ is the Green's function for outgoing waves pertaining to the full Hamiltonian H and $G_0^{(+)}$ is the Green's function pertaining to the free particle Hamiltonian.

The interaction potential $\mathcal{V}$ of two linear molecules may be split into a part which depends only on the distance r of the centers of mass of both molecules (spherical part) and a part which depends on the orientations of the molecules relative to this vector $\boldsymbol{x}$ as well (nonspherical part). The nonspherical part is assumed to be small compared with the spherical part of the interaction (small nonsphericity). It is convenient to write the intermolecular potential in the form

$$\mathcal{V} = V + \varepsilon v , \qquad (1.4)$$

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where the spherical part V and the nonspherical part v are of the same order of magnitude and ε essentially measures the nonsphericity.

The expansion of (1.3) in powers of ε (cf. Ref. [1]) yields

$$\mathcal{T} = T^{(0)} + \varepsilon\, T^{(1)} + \varepsilon^2\, T^{(2)} + \dots \tag{1.5}$$

where the first few $T^{(i)}$, in a representation-invariant notation, are given by

$$T^{(0)} = V(1 + G^{(+)} V), \tag{1.6a}$$

$$T^{(1)} = (1 + V\, G^{(+)})\, v\, (1 + G^{(+)} V), \tag{1.6b}$$

$$T^{(2)} = (1 + V\, G^{(+)})\, v\, G^{(+)}\, v\, (1 + G^{(+)} V). \tag{1.6c}$$

In (1.6) $G^{(+)}$ is the Green's operator

$$(E - H_0 - V + i\,\eta)^{-1}$$

for outgoing waves for the scattering process by the spherical potential V alone. The free particle Hamiltonian is denoted by H_0. Notice, that the expansion of $\mathcal{T}$ linear in ε in essence is the representation-invariant form of an ordinary distorted wave Born approximation [17] (DWBA).

Internal states of linear molecules (which are assumed to be in the vibrational and electronic ground states) are specified by the rotational and magnetic quantum numbers j and m. The internal rotational states are denoted by $|\, j\, m\rangle$. The projection operator into the j-subspace can now be defined by

$$P^j = \sum_m |\, j\, m\rangle \langle j\, m\,| \,. \tag{1.7}$$

The corresponding two particle projection operator is then

$$P^{j_1 j_2} = P^{j_1} \otimes P^{j_2}, \tag{1.8}$$

where $\otimes$ is an outer (Kronecker) product.

The single channel scattering amplitude operator for a transition $j_1{}' + j_2{}' \rightarrow j_1 + j_2$ between molecular rotational levels can then be written in the form

$$a^{j_1 j_2,\, j_1' j_2'} = P^{j_1 j_2}\, a\, P^{j_1' j_2'}, \tag{1.9}$$

and the total scattering amplitude operator a is then

$$a = \sum_{j_1' j_2' j_1 j_2} a^{j_1 j_2,\, j_1' j_2'}, \tag{1.10}$$

since $\sum_{j_1 j_2} P^{j_1 j_2} = 1$.

For the single channel scattering amplitude Eq. (1.1) reads

$$\begin{aligned} a^{j_1 j_2,\, j_1' j_2'}(\boldsymbol{k}, \boldsymbol{k}') &= -\frac{m_{12}}{2\,\pi\,\hbar^2} \langle \boldsymbol{k}\,|\, \mathcal{T}^{j_1 j_2,\, j_1' j_2'} \,|\, \boldsymbol{k}' \rangle \\ &= -\frac{m_{12}}{2\,\pi\,\hbar^2} \{ \langle \mathbf{k} \,|\, T^{(0)} \,|\, \boldsymbol{k}' \rangle\ \delta^{j_1 j_1'}\, \delta^{j_2 j_2'}\, P^{j_1 j_2} + \varepsilon \langle \boldsymbol{k} \,|\, T^{(1)\, j_1 j_2,\, j_1' j_2'} \,|\, \boldsymbol{k}' \rangle + \dots \}\,. \end{aligned} \tag{1.11}$$

Since $T^{(0)}$ is linked with the spherical part of the molecular interaction only, it cannot induce transitions between rotational levels and magnetic substates.

On the energy shell, the magnitudes of the vectors $\boldsymbol{k}$ and $\boldsymbol{k}'$ occuring in (1.11) are connected by

$$\frac{\hbar^2 k^2}{2\, m_{12}} + E(j_1) + E(j_2) = \frac{\hbar^2 k'^2}{2\, m_{12}} + E(j_1{}') + E(j_2{}'), \tag{1.12}$$

with $E(j) = \hbar^2\, j(j+1)/2\,\Theta$ and Θ is the moment of inertia of a colliding molecule.

Observables that can be measured in a scattering experiment are bilinear in the scattering amplitude a and its adjoint $a^\dagger$. For example, the single channel differential cross section in the absence of any polarization, averaged over initial and summed over final magnetic quantum numbers, is given by

$$\begin{aligned} &\bar{\sigma}_{\text{unpol}}(j_1\, j_2, j_1{}'\, j_2{}' \,|\, k, \boldsymbol{e}, \boldsymbol{e}') \\ &= \frac{1}{(2\, j_1{}' + 1)\,(2\, j_2{}' + 1)} \frac{k}{k'} \operatorname{tr}_1 \operatorname{tr}_2 \{ a^{j_1 j_2,\, j_1' j_2'}\ (a^\dagger)^{j_1' j_2',\, j_1 j_2} \}\,. \end{aligned} \tag{1.13}$$

It is of order ε^0 for energetically elastic encounters and of order ε^2 for inelastic ones as it can be inferred from Eqs. (1.11), (1.13). Consequences for collision brackets will be discussed in § 5. Further examples of observables are discussed in detail in § 4.

§ 2. Nonspherical Interactions between Diatomic Molecules

In this section, some general features of the nonspherical interaction between linear molecules are discussed, especially for the long range attractive part. Then special attention is paid to the interaction potentials for $H_2 - H_2$ and $HD - HD$. The expansion

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[17] See e. g. chapter 12 in "Introduction to the Quantum Theory of Scattering" by L. S. RODBERG and R. M. THALER, Academic Press, New York 1967.

of the intermolecular potential in terms of polynomials which take into account the relative orientations of the molecular axes $\boldsymbol{u}^{(1)}$ and $\boldsymbol{u}^{(2)}$ (unit vectors) and the unit vector $\hat{\boldsymbol{x}}$ in the direction of the line connecting the centers of mass of both molecules is studied first. For this purpose it proves useful to introduce generalized Legendre functions $P_{ll'L}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}})$ of the three unit vectors $\boldsymbol{u}^{(1)}$, $\boldsymbol{u}^{(2)}$ and $\hat{\boldsymbol{x}}$.

For arbitrary unit vectors $\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}$ these real functions of the three rotational invariants of the three unit vectors are defined by

$$P_{ll'L}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}) = (4\pi)^{3/2} \, [(2l+1)(2l'+1)(2L+1)]^{-1/2} \, (l0, l'0 \mid L0) \cdot \sum_{mm'M} Y^*_{lm}(\boldsymbol{a}) \, Y^*_{l'm'}(\boldsymbol{b}) \, (lm, l'm' \mid LM) \, Y_{LM}(\boldsymbol{c}), \tag{2.1}$$

where the $Y_{lm}(\boldsymbol{a})$ are the usual spherical harmonics and $(lm, l'm' \mid LM)$ is a Clebsch-Gordan coefficient. Some important special cases of (2.1) are (for further properties see the appendix)

$$P_{000}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}) = 1, \tag{2.2a}$$

$$P_{l0L}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}) = P_l(\boldsymbol{a} \cdot \boldsymbol{c}) \, \delta_{lL}, \tag{2.2b}$$

$$P_{0l'L}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}) = P_{l'}(\boldsymbol{b} \cdot \boldsymbol{c}) \, \delta_{l'L}, \tag{2.2c}$$

$$P_{ll'0}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}) = (2l+1)^{-1} P_l(\boldsymbol{a} \cdot \boldsymbol{b}) \, \delta_{ll'}. \tag{2.2d}$$

The expansion of the nonspherical interaction potential $\mathcal{V}$ can be written as [21]

$$\mathcal{V}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x}) = \sum_{ll'L} V_{ll'L}(r) \, P_{ll'L}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}}). \tag{2.3}$$

The functions $V_{ll'L}(r)$ may be decomposed into a sum of a repulsive short range part $V^{\mathrm{sr}}_{ll'}(r)$ and an attractive long range part $V^{\mathrm{lr}}_{ll'}(r)$. Little information is available regarding the short range part except in the case of the H_2 – He interaction where ab initio calculations have been performed by ROBERTS [18].

The long range part of (2.3),

$$\mathcal{V}^{\mathrm{lr}}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x}) = \sum_{ll'L} V^{\mathrm{lr}}_{ll'L}(r) \, P_{ll'L}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}})$$

is known to some extent since it is related to the electric multipole moments and the polarizabilities and hyperpolarizabilities of the molecules. Here we follow the comprehensive review article of BUCKINGHAM [19] and write

$$\mathcal{V}^{\mathrm{lr}} = \mathcal{V}_{\mathrm{disp}} + \mathcal{V}_{\mathrm{ind}} + \mathcal{V}_{\mathrm{elec}}. \tag{2.4}$$

The dispersion energy $\mathcal{V}_{\mathrm{disp}}$ stems from the induced multipole-multipole interaction, the induction energy $\mathcal{V}_{\mathrm{ind}}$ from the interaction of the static multipoles with the induced ones and V_{elec} is the electrostatic interaction of the permanent multipole moments of the particles.

If one takes into account only the induced dipole-dipole term in $\mathcal{V}_{\mathrm{disp}}$ and decomposes the polarizability tensor of a linear molecule into its isotropic and anisotropic part according to [20]

$$\alpha_{\mu\nu} = \alpha \, \delta_{\mu\nu} + (\alpha_{\parallel} - \alpha_{\perp}) \, \overline{u_\mu u_\nu}, \tag{2.5}$$

with $\alpha = \frac{1}{3}(2\alpha_\perp + \alpha_\parallel)$, then one gets [21a]

$$\mathcal{V}_{\mathrm{disp}}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x}) = -A \, \alpha_1 \alpha_2 r^{-6}[1 + \tfrac{1}{3}\gamma^{(1)} P_2(\boldsymbol{u}^{(1)} \cdot \hat{\boldsymbol{x}}) + \tfrac{1}{3}\gamma^{(2)} P_2(\boldsymbol{u}^{(2)} \cdot \hat{\boldsymbol{x}}) + \tfrac{1}{9}\gamma^{(1)}\gamma^{(2)} (6 P_{224}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}}) + \tfrac{1}{5} P_2(\boldsymbol{u}^{(1)} \cdot \boldsymbol{u}^{(2)}) - \tfrac{1}{3} P_{222}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}}))], \tag{2.6a}$$

or, written in Cartesian notation,

$$\mathcal{V}_{\mathrm{disp}}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}}) = -A \, \alpha_1 \alpha_2 r^{-6}[1 + \tfrac{1}{2} \overline{\hat{x}_\mu \hat{x}_\nu} \, (\gamma^{(1)} \overline{u^{(1)}_\mu u^{(1)}_\nu} + \gamma^{(2)} \overline{u^{(2)}_\mu u^{(2)}_\nu}) + \tfrac{3}{2} \gamma^{(1)} \gamma^{(2)} \overline{\hat{x}_\mu \hat{x}_\nu} \, \overline{\hat{x}_\lambda \hat{x}_\varkappa} \, \overline{u^{(1)}_\mu u^{(1)}_\lambda} \, \overline{u^{(2)}_\nu u^{(2)}_\varkappa}]. \tag{2.6b}$$

In (2.6a, b) A is a typical energy [19] and $\gamma^{(i)}$ is the ratio

$$\frac{\alpha^{(i)}_{\parallel} - \alpha^{(i)}_{\perp}}{\alpha^{(i)}}.$$

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[20] Cartesian indices are denoted by Greek subscripts, the summation convention is used and the symbol $\overline{}$ refers to the irreducible (symmetric traceless) part of a tensor, e. g. $\overline{a_\mu b_\nu} = \frac{1}{2}(a_\mu b_\nu + b_\mu a_\nu) - \frac{1}{3} \boldsymbol{a} \cdot \boldsymbol{b} \, \delta_{\mu\nu}$.

[21] Note, that the $P_{ll'L}(u^{(1)}, u^{(2)}, \hat{x})$ are functions of the three angles χ_1, χ_2, φ of Ref. [1], if $\hat{x}$ is taken as polar axis.

[21a] Note, that the vector $\boldsymbol{x}$ occurring in Eqs. (2.6) – (2.9b) is parallel to the line connecting the geometrical centers of the interacting molecules and coincides with the line connecting the centers of mass only for homonuclear diatomic molecules.

For H_2, γ is about[22, 23] 1/3 so that terms containing products $\gamma^{(1)}\gamma^{(2)}$ in (2.6 a, b) may, in first approximation, be neglected compared with those linear in $\gamma^{(1,2)}$.

The induction energy $\mathcal{V}_{\text{ind}}$ for molecules with dipole moments $\boldsymbol{d}_1 = d_1 \boldsymbol{u}^{(1)}$, $\boldsymbol{d}_2 = d_2 \boldsymbol{u}^{(2)}$ is given (to lowest order in the polarizabilities) by

$$\begin{aligned}\mathcal{V}_{\text{ind}}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x}) = &-\alpha_1 d_2^{\,2} r^{-6} [1 + P_2(\boldsymbol{u}^{(2)} \cdot \hat{\boldsymbol{x}}) + \gamma^{(1)} (\tfrac{1}{3} P_2(\boldsymbol{u}^{(1)} \cdot \hat{\boldsymbol{x}}) \\ &+ 2 P_{224}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}}) + \tfrac{1}{15} P_2(\boldsymbol{u}^{(1)} \cdot \boldsymbol{u}^{(2)}) - \tfrac{1}{9} P_{222}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}}))] \\ &+ (1,2) \text{ interchanged.}\end{aligned} \tag{2.7}$$

Finally, the interaction of the permanent multipoles may be written as

$$\mathcal{V}_{\text{elec}} = \mathcal{V}_{\text{d, d}} + \mathcal{V}_{\text{d, q}} + \mathcal{V}_{\text{q, q}} \quad + \text{higher order multipole terms.}$$

The dipole-dipole interaction is

$$\mathcal{V}_{\text{d, d}}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x}) = -3\, d_1 d_2 r^{-3}\, \overline{u_\mu^{(1)} u_\nu^{(2)}}\, \overline{\hat{x}_\mu \hat{x}_\nu} = -3\, d_1 d_2 r^{-3} P_{112}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}}), \tag{2.8}$$

the dipole-quadrupole terms are

$$\begin{aligned}\mathcal{V}_{\text{d, q}}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x}) &= -\tfrac{45}{2} r^{-4} d_2 Q_1 u_\mu^{(2)}\, \overline{u_\nu^{(1)} u_\lambda^{(1)}}\, \overline{\hat{x}_\mu \hat{x}_\nu \hat{x}_\lambda} - (1,2) \text{ interchanged} \\ &= 5 r^{-4} d_2 Q_1 P_{123}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}}) \qquad - (1,2) \text{ interchanged,}\end{aligned} \tag{2.9a}$$

and the quadrupole-quadrupole interaction is

$$\mathcal{V}_{\text{q, q}}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x}) = \tfrac{105}{16} Q_1 Q_2 r^{-5}\, \overline{u_\mu^{(1)} u_\nu^{(1)}}\, \overline{u_\lambda^{(2)} u_\varkappa^{(2)}}\, \overline{\hat{x}_\mu \hat{x}_\nu \hat{x}_\lambda \hat{x}_\varkappa} = \tfrac{35}{12} Q_1 Q_2 r^{-5} P_{224}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}}). \tag{2.9b}$$

The term (2.9b) occurs for all linear molecules (Q is the value of the molecular quadrupole moment) while the terms [(2.7), (2.8), (2.9a)] are present for polar molecules only (e. g. HCl, HCN, OCS).

For the interaction of linear molecules with monatomics, Eqs. (2.3), (2.6), (2.7) take a simpler form. In particular, if the particle labelled 2 is monatomic, l' and $\gamma^{(2)}$ are equal to zero. This implies, that only ordinary Legendre polynomials $P_l(\boldsymbol{u}^{(1)} \cdot \hat{\boldsymbol{x}})$ occur.

If the nonspherical part of (2.3) is small compared with the spherical part, it is useful to make the following decomposition:

$$\mathcal{V}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x}) = V(r) + \sum_L \sum_{(l,l') \neq (0,0)} \varepsilon_{ll'L} U_{ll'L}(r) P_{ll'L}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \hat{\boldsymbol{x}}) \tag{2.10}$$

where the $U_{ll'L}(r)$ are of the same order of magnitude as $V(r) = V_{000}(r)$. The $\varepsilon_{ll'L}$ are the nonsphericity parameters belonging to the corresponding generalized Legendre functions. In certain important cases (H_2, D_2, HD) it may be sufficient to take into account only one nonzero value for l and l'.

As examples the hydrogen molecules H_2 and HD are considered. For the $H_2 - H_2$ interaction the terms with $L = 2$, $l = 0$, $l' = 2$ and vice versa are the most important ones (the others may be neglected). Then the $H_2 - H_2$ interaction has the form

$$\mathcal{V}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x}) = V(r) + \varepsilon\, v_{20}(r) [P_2(\boldsymbol{u}^{(1)} \cdot \hat{\boldsymbol{x}}) + P_2(\boldsymbol{u}^{(2)} \cdot \hat{\boldsymbol{x}})], \tag{2.11}$$

where $\varepsilon = \varepsilon_{202}$ and $v_{20}(r) = U_{202}(r) = U_{022}(r)$. Potential functions $V(r)$ and $v_{20}(r)$ have been given by TAKAYANAGI[24], TAKAYANAGI and NIBLETT[25], and the mean nonsphericity parameter ε is about 0.07.

In calculations with HD a modified Morse potential has been used by TAKAYANAGI[24], and SLUIJTER[3] and TAKAYANAGI calculated the rotational relaxation coefficient for the $0 + 0 \rightarrow 1 + 0$ transition in HD. This ad hoc potential had the form[25a]

$$\mathcal{V}(\boldsymbol{u}^{(1)}, \boldsymbol{x}) = V(r) + \varepsilon\, v_{10}(r) P_1(\boldsymbol{u}^{(1)} \cdot \hat{\boldsymbol{x}}), \tag{2.12}$$

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[25a] The interaction potential for HD—HD is assumed to be the same as for H_2—H_2 if it is expressed as function of the vector connecting the geometrical midpoints of the molecules. Rewriting the H_2—H_2 potential as given in Ref. [24] for HD—HD as a function of the vector parallel to the line connecting the centers of mass of the HD molecules and performing an average over the orientation of molecule "2" one obtains (2.12, 2.13).

where

$$V(r) = D\{\exp[-2\,\alpha(r-r_0)] - 2\exp[-\alpha(r-r_0)]\}\,, \tag{2.13a}$$

and

$$\varepsilon\, v_{10}(r) = D\{\beta_1 \exp[-2\,\alpha(r-r_0)] - \beta_2 \exp[-\alpha(r-r_0)]\}\,. \tag{2.13b}$$

Higher order Legendre polynomials have been neglected. The constants D, r_0, α, β_1, β_2 may be taken from Ref. [3]. A simple generalization of (2.12) to the case where both HD molecules are allowed to jump into excited rotational states (but not simultaneously) consists in replacing $P_1(\boldsymbol{u}^{(1)}\cdot\hat{\boldsymbol{x}})$ by the symmetrized term $[P_1(\boldsymbol{u}^{(1)}\cdot\hat{\boldsymbol{x}}) - P_1(\boldsymbol{u}^{(2)}\cdot\hat{\boldsymbol{x}})]$ where the minus sign appears because $\hat{\boldsymbol{x}} = \hat{\boldsymbol{x}}_{12} = -\hat{\boldsymbol{x}}_{21}$.

The ratio $v_{10}(r)/V(r)$ changes with r and is different for the short range and long range part of the interaction. For $r \lesssim 4\,a_0$ (a_0 is the Bohr radius) it is about 0.45 and for $r \gtrsim 8\,a_0$ it is about 0.21. A mean nonsphericity parameter may thus be given by $\varepsilon \approx 0.3$. The nonsphericity of the HD – HD interaction is thus nearly one order of magnitude larger than that of the $H_2 - H_2$ interaction. Terms proportional to ε^2 in the scattering $\mathcal{T}$ matrix could give a non-negligible contribution so that a first order DWBA calculation may not be sufficient, except for order-of-magnitude considerations.

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§ 3. Angular Momentum Dependence of the Scattering Amplitude

To obtain the operator form of the rotational angular momentum dependence of the scattering amplitude linear in the nonsphericity, the "spin operator" notation of the spherical harmonics for a transition from a rotational level j' to a level j is needed. Introducing the spherical tensor operators $T^{jj'}_{lm}$, defined by

$$T^{jj'}_{lm} = \sum_{m'}\sum_{m''} (-)^{j-m''} (j'\,m', j-m''\,|\,l\,m)\,|\,j\,m''\rangle\langle j'\,m'|\,, \tag{3.1}$$

one has

$$[Y^*_{lm}(\boldsymbol{u})]^{jj'} = P^j\, Y^*_{lm}(\boldsymbol{u})\, P^{j'} = \sqrt{\frac{2\,j+1}{4\,\pi}}\,(j\,0, l\,0\,|\,j'\,0)\; T^{jj'}_{lm}\,. \tag{3.2}$$

The Clebsch-Gordan coefficients are denoted by $(j\,m, j'\,m'\,|\,J\,M)$. For further properties of the $T^{jj'}_{lm}$ see Ref. [1]. From (3.2) and (2.1) the operator form of the generalized Legendre functions and, using (2.10), of the whole nonspherical potential can be obtained, viz.,

$$[\mathcal{V}(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x})]^{j_1 j_2,\, j_1' j_2'} = V(r)\, P^{j_1 j_2}\, \delta^{j_1 j_1'}\, \delta^{j_2' j_2'} + \sum_L \sum_{(l,l') \neq (0,0)} \varepsilon_{ll'L}\, U_{ll'L}(r)\, P^{j_1 j_2, j_1' j_2'}_{ll'L}\,, \tag{3.3}$$

with the scalar two particle operator

$$P^{j_1 j_2, j_1' j_2'}_{ll'L} = (4\,\pi)^{1/2} \sqrt{\frac{(2\,j_1+1)\,(2\,j_2+1)}{(2\,l+1)\,(2\,l'+1)\,(2\,L+1)}}\,(l\,0, l'\,0\,|\,L\,0)\,(j_1\,0, l\,0\,|\,j_1'\,0)\,(j_2\,0, l'\,0\,|\,j_2'\,0) \cdot \sum_{m,m',M} (l\,m, l'\,m'\,|\,L\,M)\; T^{j_1 j_1'}_{lm}\; T^{j_2 j_2'}_{l'm'}\; Y_{LM}(\hat{\boldsymbol{x}})\,. \tag{3.4}$$

As a special case, if one of the particles, viz. particle 2, is a monatomic, then $j_2 = j_2' = 0$ and $l' = m' = 0$ in (3.4).

For a DWBA calculation of $T^{(1)}$, the part of the $\mathcal{T}$ matrix linear in ε, with a partial wave expansion (which shall be given in a forthcoming paper), the spherical tensor form appears to be the most convenient one. However, it is also possible to express the interaction in terms of Cartesian tensor operators $T^{jj'}_{\mu_1\ldots\mu_l}$, defined by the equality of scalar products in spherical and Cartesian form [9]

$$\sqrt{4\,\pi}\,\sum_m T^{jj'}_{lm}\, Y_{lm}(\hat{\boldsymbol{x}}) = \sqrt{\frac{(2\,l+1)\,!!}{l\,!}}\; T^{jj'}_{\mu_1\ldots\mu_l}\, \overline{\hat{x}_{\mu_1} \ldots \hat{x}_{\mu_l}}\,. \tag{3.5}$$

Here, in analogy with (3.2), the operator form of the tensor $\overline{u_{\mu_1} \ldots u_{\mu_l}}$ is [9]

$$\overline{u_{\mu_1} \ldots u_{\mu_l}}^{\,jj'} = \sqrt{\frac{l\,!}{(2\,l+1)\,!!}}\; \sqrt{2\,j+1}\,(j\,0, l\,0\,|\,j'\,0)\; T^{jj'}_{\mu_1\ldots\mu_l}\,. \tag{3.6}$$

Equation (3.4) can also be written in Cartesian form by using (3.6) and the relation (A1) of the appendix.

In the case of $j = j'$ (elastic scattering) the tensor operator $T^{jj}_{\mu_1\ldots\mu_l}$ is related to the well known hermitian tensor operator for spin j, $P^j\, \overline{J_{\mu_1} \ldots J_{\mu_l}}\, P^j$, which is built up from the vector spin operators J_μ (with $J_\mu J_\nu - J_\nu J_\mu = i\, \varepsilon_{\mu\nu\lambda}\, J_\lambda$) by

$$T^{jj}_{\mu_1\dots\mu_l} = P^j\, \overline{J_{\mu_1}\dots J_{\mu_l}}\, P^j \cdot \left[\frac{(2\,l+1)\,!\,!}{l!}\right]^{1/2} \frac{1}{\sqrt{2\,j+1}} \cdot (j_{(0)}\dots j_{(l-1)})^{-1}\,, \tag{3.7}$$

with

$$j_{(l)} = \sqrt{j(j+1) - \tfrac{1}{2}\,l(\tfrac{1}{2}\,l+1)}\,. \tag{3.8}$$

From (1.6b) one infers that in the approximation linear in the nonsphericity (first order DWBA) $T^{(1)}$ has the same angular momentum dependence as the nonspherical interaction v which is given by the second term of the right hand side of Eq. (3.3). Note, that simultaneous transitions in both molecules can occur only if both l and l' are different from zero. On the other hand, for H_2, HD the most important terms seem to be those with one of l or l' being zero so that only one of these molecules undergoes a transition in a collision.

For a simple nonspherical potential

$$\begin{aligned} v(\boldsymbol{u}^{(1)}, \boldsymbol{u}^{(2)}, \boldsymbol{x}) &= \varepsilon\, v_{l0}(r)\,[P_l(\boldsymbol{u}^{(1)}\cdot\hat{\boldsymbol{x}}) + (-)^l P_l(\boldsymbol{u}^{(2)}\cdot\hat{\boldsymbol{x}})] \\ &= \varepsilon\, v_{l0}(r)\,\frac{(2\,l-1)\,!\,!}{l!}\,\overline{\hat{x}_{\mu_1}\dots\hat{x}_{\mu_l}}\,(\overline{u^{(1)}_{\mu_1}\dots u^{(1)}_{\mu_l}} + (-)^l\,\overline{u^{(2)}_{\mu_1}\dots u^{(2)}_{\mu_l}}) \end{aligned} \tag{3.9}$$

[the factor $(-)^l$ is necessary, because $\hat{\boldsymbol{x}} \equiv \hat{\boldsymbol{x}}_{12} = -\hat{\boldsymbol{x}}_{21}$ and the potential must be symmetric with respect to an interchange of 1 and 2] the scattering amplitude is, to terms linear in ε

$$a = a_{\text{sph}} + \varepsilon \sum_{j_1 j_2 j_1' j_2'} a^{j_1 j_2, j_1' j_2'}_{\text{nonsph}}\,. \tag{3.10}$$

A matrix element of $a^{j_1 j_2, j_1' j_2'}_{\text{nonsph}}$ can be obtained from (1.1) and (1.6b):

$$\begin{aligned} (a^{j_1 j_2, j_1' j_2'}_{\text{nonsph}})_{m_1 m_2, m_1' m_2'} = &- \frac{m_{12}}{2\,\pi\,\hbar^2}\,\frac{(2\,l-1)\,!\,!}{l!}\,\langle \boldsymbol{k}, j_1\,m_1, j_2\,m_2 |\, [1 + V(E - H_{\text{int}} - K - V + i\,\eta)^{-1}] \\ &v_{l0}\,\overline{\hat{x}_{\mu_1}\dots\hat{x}_{\mu_l}}\,(\overline{u^{(1)}_{\mu_1}\dots u^{(1)}_{\mu_l}} + (-)^l\,\overline{u^{(2)}_{\mu_1}\dots u^{(2)}_{\mu_l}})\,[1 + (E - H_{\text{int}} - K - V + i\,\eta)^{-1}\,V]\,|\, j_1'\,m_1', j_2'\,m_2', \boldsymbol{k}'\rangle\,. \end{aligned} \tag{3.11}$$

In Eq. (3.11), the states $|\boldsymbol{k}\rangle$ and $|\boldsymbol{k}'\rangle$ are plane wave states, K is the operator for the relative kinetic energy, H_{int} is the internal Hamiltonian and E is the total energy for noninteracting particles.

Since

$$H_{\text{int}}\,|\, j_1\,m_1, j_2\,m_2\rangle = (E(j_1) + E(j_2))\,|\, j_1\,m_1, j_2\,m_2\rangle\,, \tag{3.12}$$

and

$$E - E(j_1) - E(j_2) = \frac{\hbar^2\,k^2}{2\,m_{12}}\,, \qquad E - E(j_1') - E(j_2') = \frac{\hbar^2\,k'^2}{2\,m_{12}} \tag{3.13}$$

and V, K, and v_{l0} do not act on internal states, Eq. (3.11) can be rewritten in the form

$$\begin{aligned} (a^{j_1 j_2, j_1' j_2'}_{\text{nonsph}})_{m_1 m_2, m_1' m_2'} = &\frac{(2\,l-1)\,!\,!}{l!}\,A_{\mu_1\dots\mu_l}(\boldsymbol{k}, \boldsymbol{k}')\,\{\langle j_1\,m_1 |\, \overline{u^{(1)}_{\mu_1}\dots u^{(1)}_{\mu_l}}\,|\, j_1'\,m_1'\rangle\,\delta_{j_2 j_2'}\,\delta_{m_2 m_2'} \\ &+ (-)^l \langle j_2\,m_2 |\, \overline{u^{(2)}_{\mu_1}\dots u^{(2)}_{\mu_l}}\,|\, j_2'\,m_2'\rangle\,\delta_{j_1 j_1'}\,\delta_{m_1 m_1'}\}\,. \end{aligned} \tag{3.14}$$

In Eq. (3.14) the l-th rank tensor $A_{\mu_1\dots\mu_l}(\boldsymbol{k}, \boldsymbol{k}')$ is given by

$$A_{\mu_1\dots\mu_l}(\boldsymbol{k}, \boldsymbol{k}') = -\frac{m_{12}}{2\,\pi\,\hbar^2}\,\langle \chi^{(-)}_{\boldsymbol{k}} |\, v_{l0}\,\overline{\hat{x}_{\mu_1}\dots\hat{x}_{\mu_l}}\,|\, \chi^{(+)}_{\boldsymbol{k}'}\rangle\,, \tag{3.15}$$

where the states

$$|\chi^{(\pm)}_{\boldsymbol{k}}\rangle = \left[1 + \left(\frac{\hbar^2\,k^2}{2\,m_{12}} - K - V \pm i\,\eta\right)^{-1} V\right] |\boldsymbol{k}\rangle \tag{3.16}$$

are the "distorted wave" states[17] which are solutions of the scattering problem for the spherical interaction V with the boundary condition of plane waves + outgoing and ingoing spherical waves, respectively, at infinity. Using Eqs. (3.6), (3.10), (3.14) one obtains

$$\begin{aligned} a^{j_1 j_2, j_1' j_2'}_{\text{nonsph}}(\boldsymbol{k}, \boldsymbol{k}') = &\sqrt{\frac{(2\,l-1)\,!\,!}{(2\,l+1)\,l!}}\,A_{\mu_1\dots\mu_l}(\boldsymbol{k}, \boldsymbol{k}') \\ &\cdot\{\sqrt{2\,j_1+1}\,(j_1\,0, l\,0\,|\, j_1'\,0)\,T^{j_1 j_1'}_{\mu_1\dots\mu_l}\,\delta^{j_2 j_2'}\,P^{j_2} + (-)^l \sqrt{2\,j_2+1}\,(j_2\,0, l\,0\,|\, j_2'\,0)\,T^{j_2 j_2'}_{\mu_1\dots\mu_l}\,\delta^{j_1 j_1'}\,P^{j_1}\}\,. \end{aligned} \tag{3.17}$$

On the energy shell the magnitudes of $\boldsymbol{k}$ and $\boldsymbol{k}'$ are connected by Eq. (1.12).

The tensor $A_{\mu_1 \dots \mu_l}(\boldsymbol{k}, \boldsymbol{k}')$ can be expanded into a sum of the $(l+1)$ irreducible l-th rank tensors which can be constructed from the unit vectors $\boldsymbol{e}$ and $\boldsymbol{e}'$:

$$A_{\mu_1 \dots \mu_l}(\boldsymbol{k}, \boldsymbol{k}') = a_0(k, k', \boldsymbol{e}\cdot\boldsymbol{e}')\, \overline{e_{\mu_1} \dots e_{\mu_l}} + a_1(k, k', \boldsymbol{e}\cdot\boldsymbol{e}')\, \overline{e'_{\mu_1} e_{\mu_2} \dots e_{\mu_l}}$$
$$+ \dots + a_{l-1}(k, k', \boldsymbol{e}\cdot\boldsymbol{e}')\, \overline{e_{\mu_1} e'_{\mu_2} \dots e'_{\mu_l}} + a_l(k, k', \boldsymbol{e}\cdot\boldsymbol{e}')\, \overline{e'_{\mu_1} \dots e'_{\mu_l}}\,. \tag{3.18}$$

The angle of deflection ϑ is defined by $\cos\vartheta = \boldsymbol{e}\cdot\boldsymbol{e}'$ (cf. § 5).

Equations (3.17) and (3.18) are consequences of rotational invariance. For completeness let us also indicate the symmetries of the scattering amplitude which result from invariance under time reversal and under space reflection. The Cartesian angular momentum vector $\boldsymbol{J}$ and the Cartesian unit vector $\boldsymbol{u}$ are used for the description of intramolecular mechanics. The vector $\boldsymbol{u}$ is restricted by the constraints

$$\boldsymbol{u}\cdot\boldsymbol{u} = 1, \qquad \boldsymbol{u}\cdot\boldsymbol{J} = 0\,. \tag{3.19}$$

Thus, it has only one free component which together with $\boldsymbol{J}$ gives four independent variables equivalent to the canonical set ϑ, φ, p_ϑ, p_φ of the internal spherical coordinates of the rotator. According to the physical meaning of $\boldsymbol{J}$ as the operator of infinitesimal rotation, its commutator with $\boldsymbol{u}$ is

$$[J_\mu, u_\nu]_- = i\,\varepsilon_{\mu\nu\lambda}\, u_\lambda\,. \tag{3.20}$$

The constraints (3.19) are compatible with (3.20). The same commutation rule is valid for $\boldsymbol{J}$ itself, whereas the components of $\boldsymbol{u}$ commute:

$$[J_\mu, J_\nu]_- = i\,\varepsilon_{\mu\nu\lambda}\, J_\lambda; \qquad [u_\mu, u_\nu]_- = 0\,.$$

Now, these commutation rules are invariant under "time reversal", i. e. under replacing $\vec{\boldsymbol{J}}$, $\vec{\boldsymbol{u}}$ by $-\overleftarrow{\boldsymbol{J}}$, $\overleftarrow{\boldsymbol{u}}$. The arrows directed to the left mean that in time reversed products the sequence of factors has to be reversed (reading from right to left). If the total Hamiltonian of two molecules, translational motion included, has this same invariance property as the commutation rules it is called invariant under time reversal. Obviously, this symmetry again appears in the scattering amplitude (an operator with respect to intramolecular states):

$$a(E, \boldsymbol{e}, \boldsymbol{e}', \vec{\boldsymbol{J}}_1, \vec{\boldsymbol{u}}_1, \vec{\boldsymbol{J}}_2, \vec{\boldsymbol{u}}_2)$$
$$= a(E, -\boldsymbol{e}', -\boldsymbol{e}, -\overleftarrow{\boldsymbol{J}}_1, \overleftarrow{\boldsymbol{u}}_1, -\overleftarrow{\boldsymbol{J}}_2, \overleftarrow{\boldsymbol{u}}_2)\,. \tag{3.21}$$

This is the general expresison of the time reversal invariance.

Which are the ensueing symmetries of the more specialised quantities $A_{\mu_1 \dots \mu_l}$ and a_i of (3.18)? After (3.10) and (3.14) one has

$$a_{\text{nonsph}}(E, \boldsymbol{e}, \boldsymbol{e}', \vec{\boldsymbol{J}}_1, \vec{\boldsymbol{u}}_1, \vec{\boldsymbol{J}}_2, \vec{\boldsymbol{u}}_2)$$
$$= \frac{(2\,l-1)\,!!}{l!} \sum_{j_1} \cdot\cdot \sum_{j_2'} \{A_{\mu_1 \dots \mu_l}(K_{j_1 j_2}, K_{j_1' j_2'}, \boldsymbol{e}, \boldsymbol{e}') \cdot P^{j_1 j_2} (\overline{u^{(1)}_{\mu_1} \dots u^{(1)}_{\mu_l}} + (-)^l\, \overline{u^{(2)}_{\mu_1} \dots u^{(2)}_{\mu_l}})\, P^{j_1' j_2'}\}\,.$$

Here

$$K_{j_1 j_2} = E - E(j_1) - E(j_2),\; K_{j_1' j_2'} = E - E(j_1') - E(j_2')$$

are the relative kinetic energies. The time reversal operation yields

$$a_{\text{nonsph}}(E, -\boldsymbol{e}', -\boldsymbol{e}, -\overleftarrow{\boldsymbol{J}}_1, \overleftarrow{\boldsymbol{u}}_1, -\overleftarrow{\boldsymbol{J}}_2, \overleftarrow{\boldsymbol{u}}_2) = \frac{(2\,l-1)\,!!}{l!} \sum_{j_1} \cdots \sum_{j_2'} \{A_{\mu_1 \dots \mu_l}(K_{j_1 j_2}, K_{j_1' j_2'}, -\boldsymbol{e}', -\boldsymbol{e})$$
$$P^{j_1' j_2'} (\overline{u^{(1)}_{\mu_1} \dots u^{(1)}_{\mu_l}} + (-1)^l\, \overline{u^{(2)}_{\mu_1} \dots u^{(2)}_{\mu_l}})\, P^{j_1 j_2}\}\,,$$

or, by renaming the indices $j_1 \dots j_2{}'$:

$$a_{\text{nonsph}}(E, -\boldsymbol{e}', -\boldsymbol{e}, -\overleftarrow{\boldsymbol{J}}_1, \overleftarrow{\boldsymbol{u}}_1, -\overleftarrow{\boldsymbol{J}}_2, \overleftarrow{\boldsymbol{u}}_2) = \frac{(2\,l-1)\,!!}{l!} \sum_{j_1} \cdots \sum_{j_2'} \{A_{\mu_1 \dots \mu_l}(K_{j_1' j_2'}, K_{j_1 j_2}, -\boldsymbol{e}', -\boldsymbol{e})$$
$$P^{j_1 j_2}(\dots)\, P^{j_1' j_2'}\}\,.$$

Equating these expressions, term by term, according to the time reversal invariance (3.21) yields the symmetry

$$A_{\mu_1 \dots \mu_l}(K_{j_1 j_2}, K_{j_1' j_2'}, \boldsymbol{e}, \boldsymbol{e}') = A_{\mu_1 \dots \mu_l}(K_{j_1' j_2'}, K_{j_1 j_2}, -\boldsymbol{e}', -\boldsymbol{e})\,. \tag{3.22}$$

Finally, by decomposing the A's after (3.18), Eq. (3.22) is rewritten with an obvious abbreviation

$$\sum_{i=0}^{l} a_i(K_{j_1 j_2}, K_{j_1' j_2'}, \vartheta) \left(\overline{(e^{l-i}\, e'^{i})}\right)_{\mu_1 \dots \mu_l} = \sum_i a_i(K_{j_1' j_2'}, K_{j_1 j_2}, \vartheta) \left(\overline{((-e')^{l-i}\, (-e)^{i})}\right)_{\mu_1 \dots \mu_l}$$
$$= (-1)^l \sum_i a_{l-i}(K_{j_1' j_2'}, K_{j_1 j_2}, \vartheta) \left(\overline{(e^{l-i}\, e'^{i})}\right)_{\mu_1 \dots \mu_l},$$

or, term by term

$$a_i(K_{j_1 j_2}, K_{j_1' j_2'}, \vartheta) = (-1)^l a_{l-i}(K_{j_1' j_2'}, K_{j_1 j_2}, \vartheta). \qquad (3.23)$$

This is the most detailed expression for the time reversal invariance in the case considered.

Similar remarks, even simpler, apply to the invariance under space reflection (parity conservation). The relevant property of the commutation rules is their invariance under replacing $\vec{\boldsymbol{J}}, \vec{\boldsymbol{u}}$ by $\vec{\boldsymbol{J}}, -\vec{\boldsymbol{u}}$ and, for the translational motion, replacing $\vec{\boldsymbol{x}}, \vec{\boldsymbol{p}}$ by $-\vec{\boldsymbol{x}}, -\vec{\boldsymbol{p}}$. Again, from reflection invariance of the total Hamiltonian follows

$$a(E, \boldsymbol{e}, \boldsymbol{e}', \vec{\boldsymbol{J}}_1, \vec{\boldsymbol{u}}_1, \vec{\boldsymbol{J}}_2, \vec{\boldsymbol{u}}_2)$$
$$= a(E, -\boldsymbol{e}, -\boldsymbol{e}', \vec{\boldsymbol{J}}_1, -\vec{\boldsymbol{u}}_1, \vec{\boldsymbol{J}}_2, -\vec{\boldsymbol{u}}_2) \qquad (3.24)$$

as the general symmetry of the scattering amplitude due to invariance under reflection. Returning to our model, i. e. interaction (3.9) treated in DWB-approximation, we obtain from (3.24) for the A's occurring in (3.15)

$$A_{\mu_1 \dots \mu_l}(K_{j_1 j_2}, K_{j_1' j_2'}, \boldsymbol{e}, \boldsymbol{e}')$$
$$= (-1)^l A_{\mu_1 \dots \mu_l}(K_{j_1 j_2}, K_{j_1' j_2'}, -\boldsymbol{e}, -\boldsymbol{e}')$$

which obviously is already fulfilled by the detailed expression (3.18). Hence, in this case invariance under reflection is already covered by rotational invariance.

Considering the examples $H_2(D_2)$ and HD, the following results can be stated:

a) For $H_2 - H_2$ the $l=2$ term in the nonspherical interaction potential is the most important one, so that $j_1 = j_1', j_1' \pm 2, j_2 = j_2'$ and (1, 2) interchanged. Then the total scattering amplitude is

$$a = a_{\text{sph}} + \frac{\varepsilon}{\sqrt{10}} \left\{ \sum_{j_1 j_2} \left[-A_{\mu\nu}^{(0)} \sqrt{\frac{(2\,j_1+1)\, j_1(j_1+1)}{4\,j_1(j_1+1)-3}}\; T_{\mu\nu}^{j_1 j_1} + A_{\mu\nu}^{(+2)} \sqrt{\frac{3\,(j_1+2)\,(j_1+1)}{2\,(2\,j_1+3)}}\; T_{\mu\nu}^{j_1+2 j_1} \right.\right.$$
$$\left.\left. + A_{\mu\nu}^{(-2)} \sqrt{\frac{3\,j_1(j_1-1)}{2\,(2\,j_1-1)}}\; T_{\mu\nu}^{j_1-2 j_1} \right] P^{j_2} + (1,2) \text{ interchanged} \right\}. \qquad (3.25)$$

The second rank tensors $A_{\mu\nu}^{(\alpha)}$ with $\alpha = 0, \pm 2$ can be written according to Eq. (3.18) as

$$A_{\mu\nu}^{(\alpha)} = a_0^{(\alpha)}\, \overline{e_\mu\, e_\nu} + a_1^{(\alpha)}\, \overline{e_\mu'\, e_\nu} + a_2^{(\alpha)}\, \overline{e_\mu'\, e_\nu'} \qquad (3.26a)$$

with

$$a^{(\alpha)}(k, \boldsymbol{e}\cdot\boldsymbol{e}') = a(k, k^{(\alpha)}, \boldsymbol{e}\cdot\boldsymbol{e}') \qquad (3.26b)$$

and with $k^{(0)} = k$ and $a_0^{(0)} = a_2^{(0)}$ (elastic scattering, cf. Ref. [1]).

b) For HD – HD the $l=1$ term seems to be most important one in the nonspherical interaction so that the selection rules $j_1 = j_1' \pm 1$, $j_2 = j_2'$ and (1, 2) interchanged hold. The total scattering amplitude is then

$$a = a_{\text{sph}} - \frac{\varepsilon}{\sqrt{3}} \left\{ \sum_{j_1 j_2} \left[A_\mu^{(+1)} \sqrt{j_1+1}\; T_\mu^{j_1+1 j_1} - A_\mu^{(-1)} \sqrt{j_1}\; T_\mu^{j_1-1 j_1} \right] P^{j_2} - (1,2) \text{ interchanged} \right\}. \qquad (3.27)$$

The vector $A_\mu^{(\alpha)}$ $(\alpha = \pm 1)$ can be written in this case as

$$A_\mu^{(\alpha)} = a_0^{(\alpha)}\, e_\mu + a_1^{(\alpha)}\, e_\mu'. \qquad (3.28)$$

§ 4. Observables in Molecular Beam Experiments with Polarized Particles

In this section molecular scattering experiments with a polarized beam are discussed. Some of the considerations here are the same as those which appear in connection with nuclear scattering and nuclear reactions with polarized nuclei [26, 27].

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a) Description of a polarized beam

Consider a beam of molecules in a specific rotational state j. It is described by a density matrix ϱ^j. If the beam is unpolarized, this density matrix is proportional to the corresponding unity matrix P^j. Polarization of the beam is, in general, associated with the occurence of different diagonal elements as well as of nondiagonal elements in the density matrix.

The various types of polarization can be classified as vector polarization, second rank tensor polarization and higher multipolarizations up to the tensor rank $l_{\max} = 2\,j$. The l-th rank multipolarization will be defined by the ensemble mean value of the l-th irreducible (either spherical or Cartesian) tensor operator. In terms of symmetric traceless Cartesian tensor operators the l-th rank multipolarization is defined by

$$\langle S^j_{\mu_1 \dots \mu_l} \rangle = \mathrm{tr}\{\varrho^j \, S^j_{\mu_1 \dots \mu_l}\}\,, \tag{4.1}$$

where, for convenience, the operators

$$S^j_{\mu_1 \dots \mu_l} = \sqrt{2\,j+1}\; T^{jj}_{\mu_1 \dots \mu_l}\,, \tag{4.2}$$

have been used instead of the $T^{jj}_{\mu_1 \dots \mu_l}$ which have been defined by Eq. (3.7). The $S^j_{\mu_1 \dots \mu_l}$ vanish identically for $l > 2\,j$ and their normalization is

$$\mathrm{tr}\,\{S^j_{\mu_1 \dots \mu_l}\, S^j_{\mu_1 \dots \mu_l}\} = (2\,l+1)\,(2\,j+1)\,. \tag{4.3}$$

This result is a consequence of the trace property

$$\mathrm{tr}\,\{S^j_{\mu_1 \dots \mu_l}\, S^j_{\nu_1 \dots \nu_{l'}}\} = (2\,j+1)\;\delta_{ll'}\,\Delta^{(l)}_{\mu_1 \dots \mu_l,\,\nu_1 \dots \nu_l}\,, \tag{4.4}$$

where $\Delta^{(l)}_{\mu_1 \dots \mu_l,\,\nu_1 \dots \nu_l}$ is an isotropic tensor which, when applied to an arbitrary l-th rank tensor, projects out the symmetric ireducible part of that tensor. For properties of the $\Delta^{(l)}$-tensor see Ref. [28]. To give an example, the first- and second rank S^j-tensors are expressed in terms of the angular momentum vectors:

$$S^j_\mu = 3\,(3\,j(j+1))^{-1/2} P^j\, J_\mu\, P^j\,, \tag{4.5a}$$

$$S^j_{\mu\nu} = \sqrt{\frac{15}{2}}\,\{j(j+1)\,[j(j+1) - \tfrac{3}{4}]\}^{-1/2}\, P^j\, \overline{J_\mu\, J_\nu}\, P^j\,. \tag{4.5b}$$

In general, the density matrix ϱ^j of a polarized beam of molecules in the rotational state j can be expanded in terms of the Cartesian tensor operators $S^j_{\mu_1 \dots \mu_l}$ as

$$\varrho^j = (2\,j+1)^{-1}[P^j + \langle S^j_\mu \rangle\, S^j_\mu + \dots + \langle S^j_{\mu_1 \dots \mu_{2j}} \rangle\, S^j_{\mu_1 \dots \mu_{2j}}]\,, \tag{4.6}$$

where $\mathrm{tr}\,\varrho^j = 1$. To check the validity of the expansion (4.6), multiply (4.6) with $S^j_{\nu_1 \dots \nu_l}$ and take the trace on both sides. Then, using the trace property (4.4), Eq. (4.1) is recovered. If the beam is unpolarized one has

$$\varrho^j = (2\,j+1)^{-1}\, P^j\,, \tag{4.7}$$

since all multipolarizations are zero.

To clarify the physical meaning of the $\langle S^j_{\mu_1 \dots \mu_l} \rangle$, the following special density matrix is considered which is diagonal with respect to a representation in terms of eigenfunctions $|\,j\,m\rangle$ of $\boldsymbol{S}^j \cdot \boldsymbol{h}$, where $\boldsymbol{h}$ is a unit vector parallel to the axis of quantization:

$$\varrho^j = \sum_m N_m\,|\,j\,m\rangle\langle j\,m\,|\,. \tag{4.8}$$

The multipolarizations can be related to the relative occupation numbers N_m ($\sum\limits_m N_m = 1$) of the magnetic substates by observing that

$$\langle S^j_{\mu_1 \dots \mu_l} \rangle = \langle S_l{}^j \rangle\, \overline{h_{\mu_1} \dots h_{\mu_l}}\,, \tag{4.9}$$

with

$$\langle S_l{}^j \rangle = (2\,l+1)\sqrt{\frac{l!}{(2\,l+1)\,!!}}\,\sum_m N_m (j\,m, l\,0\,|\,j\,m)\,. \tag{4.10}$$

For $l = 0, 1, 2$ one obtains

$$\langle S^j_0 \rangle = \sum N_m = 1\,, \tag{4.11a}$$

$$\langle S^j_1 \rangle = \left(\frac{3}{j(j+1)}\right)^{1/2} \sum m\, N_m\,, \tag{4.11b}$$

$$\langle S^j_2 \rangle = \sqrt{\frac{15}{2}}\,[j(j+1)\,[j(j+1) - \tfrac{3}{4}]]^{-1/2} \sum N_m \cdot (m^2 - \tfrac{1}{3}\, j(j+1))\,. \tag{4.11c}$$

Similar expressions, obtained by TOLHOEK and COX [28a] differ from (4.10), (4.11) by factors due to a different normalization.

b) Obversables in molecular beam experiments

Next, consider the scattering of two beams consisting of rotating molecules. The density operator in rotational angular momentum space which describes the beams before the collision is denoted with ϱ_{in}. The density operator ϱ_{fin}, describing the molecules after the collision is related to ϱ_{in} by [29, 17]

$$\varrho_{\text{fin}} = a\, \varrho_{\text{in}}\, a^\dagger\,, \tag{4.12}$$

where a is the scattering amplitude operator.

Firstly, the scattering of a polarized beam of molecules in the rotational state $j_1{}'$ on an unpolarized

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[28] S. HESS, Z. Naturforsch. **23 a**, 1095 [1968].

[28a] H. A. TOLHOEK and J. A. M. COX, Physica **19**, 101 [1953].

[29] See e. g. chapter 7 in "Collision Theory" by M. L. GOLDBERGER and K. M. WATSON, John Wiley, New York 1964.

target (which may be another beam) consisting of molecules in the rotational state $j_2{}'$ is considered. The beams are uncorrelated before the collision. Thus the density matrix which characterizes the initial ensemble can be written as the outer product

$$\varrho_{\text{in}}^{j_1{}'j_2{}'} = \varrho_{\text{in}}^{j_1{}'} \otimes \varrho_{\text{in}}^{j'_2} . \tag{4.13}$$

In Eq. (4.12) the polarized beam is described by a density matrix like (4.6) with $j = j_1{}'$ and the unpolarized target by a density matrix like (4.7) with $j = j_2{}'$. Then the conditional density matrix (i. e. depending on $j_1{}', j_2{}'$) for the molecules which are in the rotational states j_1 and j_2 after the collision is given by

$$\varrho_{\text{fin}}^{j_1 j_2} (j_1{}' \, j_2{}') = a^{j_1 j_2,\, j_1{}' j_2{}'} \, \varrho_{\text{in}}^{j_1{}' j_2{}'} \, (a^\dagger)^{j_1{}' j_2{}',\, j_1 j_2} . \tag{4.14}$$

In Eq. (4.14), the dependence of ϱ_{fin}, a, and $a^\dagger$ on $k, k', \boldsymbol{e}, \boldsymbol{e}'$ has not been indicated explicitly and will not be indicated in the following. The single channel scattering amplitude matrix has been defined in § 1.

The differential cross section for the channel $j_1{}' + j_2{}' \rightarrow j_1 + j_2$ is given by

$$\bar{\sigma}(j_1 \, j_2, j_1{}' \, j_2{}' \,|\, k, \boldsymbol{e}, \boldsymbol{e}') = \frac{k}{k'} \operatorname{tr}_1 \operatorname{tr}_2 \varrho_{\text{fin}}^{j_1 j_2} (j_1{}' \, j_2{}') . \tag{4.15}$$

Using Eqs. (4.13), (4.14), (4.15) and (4.6), (4.7), one gets

$$\bar{\sigma} = \bar{\sigma}_{\text{unpol}} (1 + \widetilde{P}_{\mu}^{(j_1{}')} \langle S_{\mu}^{j_1{}'} \rangle + \ldots + \widetilde{P}^{(j_1{}')}_{\mu_1 \ldots \mu_{2 j_1{}'}} \langle S^{j_1{}'}_{\mu_1 \ldots \mu_{2 j_1{}'}} \rangle) , \tag{4.16}$$

where $\bar{\sigma}_{\text{unpol}}$ is the differential cross section for initially unpolarized beams, given by Eq. (1.13). The quantities

$$\widetilde{P}^{(j_1{}')}_{\mu_1 \ldots \mu_l} (j_1 \, j_2, j_2{}' \,|\, k, \boldsymbol{e}, \boldsymbol{e}') = \frac{\operatorname{tr}_1 \operatorname{tr}_2 \{ a^{j_1 j_2,\, j_1{}' j_2{}'} \, S^{j_1{}'}_{\mu_1 \ldots \mu_l} \, (a^\dagger)^{j_1{}' j_2{}',\, j_1 j_2} \}}{\operatorname{tr}_1 \operatorname{tr}_2 \{ a^{j_1 j_2,\, j_1{}' j_2{}'} \, (a^\dagger)^{j_1{}' j_2{}',\, j_1 j_2} \}} \tag{4.17}$$

are the single channel "analyzing power" tensors. They are essentially a measure for the influence of the various multipolarizations of the beam on the differential cross section [30]. The analyzing power tensors vanish for a pure spherical interaction and thus they are observables which are directly related to the nonspherical part of the scattering amplitude matrix. It is stated without proof that also the total "polarized" cross section differs from the total "unpolarized" cross section and that only the even rank multipolarizations contribute to this difference (provided that the target is unpolarized).

To give an example, the observables $\bar{\sigma}_{\text{unpol}}$ and $\bar{\sigma}_{\text{unpol}} \widetilde{P}^{(j_1{}')}_{\mu\nu}$ are calculated for the $H_2 - H_2$ case up to terms linear in the nonsphericity parameter, using Eqs. (1.13), (3.25), (3.26), (4.17). The result is [see Eqs. (A.6) and (A.8)]

$$\bar{\sigma}_{\text{unpol}} (j_1{}' \, j_2{}', j_1{}' \, j_2{}') = | a_{\text{sph}} |^2 + O(\varepsilon^2) , \tag{4.18a}$$

$$\bar{\sigma}_{\text{unpol}} (j_1{}' + 2 \, j_2{}', j_1{}' \, j_2{}') = \varepsilon^2 \, \frac{k}{k^{(+2)}} \, \frac{3}{20} \, \frac{(j_1{}' + 2) \, (j_1{}' + 1)}{(2 \, j_1{}' + 3) \, (2 \, j_1{}' + 1)} \, A^{(+2)*}_{\mu\nu} \, A^{(+2)}_{\mu\nu} , \tag{4.18b}$$

$$\bar{\sigma}_{\text{unpol}} \, \widetilde{P}^{(j_1{}')}_{\mu\nu} (j_1{}' \, j_2{}', j_2{}') = - \varepsilon \sqrt{\frac{2 \, j_1{}' (j_1{}' + 1)}{5 [4 \, j_1{}' (j_1{}' + 1) - 3]}} \, \operatorname{Re} (a^*_{\text{sph}} \, A^{(0)}_{\mu\nu}) + O(\varepsilon^2) , \tag{4.19a}$$

$$\bar{\sigma}_{\text{unpol}} \, \widetilde{P}^{(j_1{}')}_{\mu\nu} (j_1{}' + 2 \, j_2{}', j_2{}') = - \varepsilon^2 \, \frac{k}{k^{(+2)}} \, \frac{3 \sqrt{30}}{140} \, \frac{(j_1{}' + 2) \, (j_1{}' + 1) \, j_1{}' (2 \, j_1{}' - 1)}{(2 \, j_1{}' + 3) \, (2 \, j_1{}' + 1)} \cdot \{ j_1{}' (j_1{}' + 1) [j_1{}' (j_1{}' + 1) - \tfrac{3}{4}] \}^{-1/2} \cdot \overline{A^{(+2)*}_{\mu\varrho} \, A^{(+2)}_{\varrho\nu}} \tag{4.19b}$$

where $k^{(+2)} = \left(\dfrac{\hbar^2 \, k^2}{2 \, m_{12}} + E(j_1{}' + 2) - E(j_1{}') \right)^{1/2}$.

Secondly, another important set of observables is obtained, if two initially unpolarized beams of molecules in the rotational states $j_1{}'$ and $j_2{}'$ are scattered and the polarization of the molecules "1" in a specific rotational state j_1 after scattering is measured. The resulting multipolarizations for the channel $j_1{}' + j_2{}' \rightarrow j_1 + j_2$ are given by

$$P^{(j_1)}_{\mu_1 \ldots \mu_l} (j_2, j_1{}' \, j_2{}' \,|\, k, \boldsymbol{e}, \boldsymbol{e}') = \frac{\operatorname{tr}_1 \operatorname{tr}_2 \{ \varrho_{\text{fin}}^{j_1 j_2} (j_1{}' \, j_2{}') \, S^{j_1}_{\mu_1 \ldots \mu_l} \}}{\operatorname{tr}_1 \operatorname{tr}_2 \, \varrho_{\text{fin}}^{j_1 j_2} (j_1{}' \, j_2{}')} = \frac{\operatorname{tr}_1 \operatorname{tr}_2 \{ a^{j_1 j_2,\, j_1{}' j_2{}'} \, (a^\dagger)^{j_1{}' j_2{}',\, j_1 j_2} \, S^{j_1}_{\mu_1 \ldots \mu_l} \}}{\operatorname{tr}_1 \operatorname{tr}_2 \{ a^{j_1 j_2,\, j_1{}' j_2{}'} \, (a^\dagger)^{j_1{}' j_2{}',\, j_1 j_2} \}} , \tag{4.20}$$

where l runs from 1 to $2 \, j_1$. Note that the sequence of a and $a^\dagger$ is different from that of Eq. (4.17). The multipolarizations (4.20) vanish again unless the scattering amplitude (and the molecular interaction) contains a nonspherical part.

In the case of $H_2 - H_2$ (and of other gases for which the linear approximation of small nonsphericity is applicable) the observables

$$\mathrm{tr}_1\, \mathrm{tr}_2 \{ a^{j_1 j_2,\, j_1' j_2'} (a^\dagger)^{j_1' j_2',\, j_1 j_2} S^{j_1}_{\mu\nu} \} \tag{4.21}$$
$$= (2\, j_1' + 1)\, (2\, j_2' + 1)\, \frac{k'}{k}\, \bar{\sigma}_{\mathrm{unpol}} (j_1\, j_2 , j_1'\, j_2')\, P^{(j_1)}_{\mu\nu}$$

which are of importance for the Senftleben-Beenakker effect (§ 5) are of order ε for energetically elastic encounters and of order ε^2 for collisional $j_1' \rightarrow j_1' \pm 2$ transitions.

As a consequence of the time reversal invariance of the molecular interaction a simple relation exists between the analyzing power tensors for scattering of a polarized by an unpolarized beam and the polarization tensors after scattering of two unpolarized beams:

$$(-1)^l\, \widetilde{P}_{\mu_1 \ldots \mu_l} (j_1\, j_2 , j_1'\, j_2' \,|\, \boldsymbol{k}, \boldsymbol{k}')$$
$$= P_{\mu_1 \ldots \mu_l} (j_1'\, j_2' , j_1\, j_2 \,|\, -\boldsymbol{k}', -\boldsymbol{k}) . \tag{4.22}$$

Other sets of observables occur if a polarized beam is scattered and the polarizations after scattering are detected. Of course, such experiments are very difficult. Nuclear scattering experiments of that kind have been discussed in Ref. [26, 27]. In kinetic gas theory (cf. § 5) observables of this type occur in collision brackets determining the diagonal relaxation coefficients of vector- and tensor polarizations of the rotational angular momentum of the molecules.

§ 5. Conclusions: Qualitative Considerations on Specific Collision Brackets

In this section, some consequences of the angular momentum dependence of the scattering amplitude of molecules with small nonspherical interaction on the collision brackets obtained from the linearized quantum-mechanical collision term [5, 31] are discussed.

a) Cross section and bulk viscosity

First the unpolarized differential cross section is considered. For elastic collisions it contains a contribution in order ε^0 which is given by $|a_{\mathrm{sph}}|^2$ and contributions in order ε^2. The inelastic differential cross section for a transition between rotational levels stems from the nonspherical part of the scattering amplitude and is at least of order ε^2.

Thus the "classical" relaxation coefficients, obtained from the linearized quantum-mechanical collision operator, which determine the isotropic values of the transport coefficients, reduce to the well-known Chapman-integrals except for terms in $O(\varepsilon^2)$ (which may be neglected). Collision brackets, however, which are related solely to the inelastic differential cross section, e. g. the translational-rotational temperature relaxation coefficient $\omega_{\mathrm{tr,\,rot}}$ are of order ε^2. In particular [2],

$$\omega_{\mathrm{tr,\,rot}} \propto \sum_{j_1 j_2 j_1' j_2'} (2\, j_1 + 1)\, (2\, j_2 + 1)$$
$$\cdot \int \exp\big(-\gamma^2 - \mathcal{E}(j_1) - \mathcal{E}(j_2) \big)\, (\Delta\mathcal{E})^2\, \gamma^3 \tag{5.1}$$
$$\cdot \{ \int \bar{\sigma}_{\mathrm{unpol}} (j_1'\, j_2' , j_1\, j_2 \,|\, \gamma \sqrt{T}, \vartheta)\, \sin\vartheta\, \mathrm{d}\vartheta \}\, \mathrm{d}\gamma ,$$

is very small compared with the relaxation coefficients which determine the isotropic values of the heat conductivity and viscosity. In (5.1), $\gamma = \hbar\, k / \sqrt{m\, k_{\mathrm{B}}\, T}$ is a dimensionless relative velocity, $\mathcal{E}(j) = E(j)/k_{\mathrm{B}}\, T$ is the dimensionless internal energy, and

$$\Delta\mathcal{E} = \mathcal{E}(j_1) + \mathcal{E}(j_2) - \mathcal{E}(j_1') - \mathcal{E}(j_2')$$

is the dimensionless internal energy transferred in a collision. Note, that the rotational relaxation coefficient $\omega_{\mathrm{rot,\,rot}}$ is proportional to $\omega_{\mathrm{tr,\,rot}}$. The bulk viscosity η_{V} is related to $\omega_{\mathrm{tr,\,rot}}$ by [2]

$$\eta_{\mathrm{V}} \propto \frac{P}{\omega_{\mathrm{tr,\,rot}}} \propto \varepsilon^{-2} . \tag{5.2}$$

Thus η_{V} will be rather large at room temperature compared with the shear viscosity which is proportional to ε^0.

The relaxation coefficient which couples the translational and internal energy flux is proportional to $\omega_{\mathrm{tr,\,rot}}$ and thus may be neglected compared with the relaxation constants of the translational and internal energy fluxes in the expression for the isotropic value of the heat conductivity [2]. Then also a simple Eucken relation holds [2].

b) Tensor polarization and Senftleben-Beenakker effect of viscosity and heat conductivity

Next, certain collision brackets of the linearized collision operator which couple "classical" (only

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[30] If suitable (from an experimental point of view) coordinate systems are introduced (cf. Refs. [27]), each of the scalar products occuring in (4.16) will, in general, contain terms up to $\cos(2\, l\, \varphi)$ and $\sin(2\, l\, \varphi)$ where l is the rank of the tensors and φ is an azimuthal angle which runs in a plane perpendicular to $\boldsymbol{e}'$.

[31] S. HESS and L. WALDMANN, Z. Naturforsch. **21 a**, 1529 [1966]; **23 a**, 1893 [1968].

velocity- and internal energy-dependent) expansion tensors with "quantum-mechanical" ones (which contain $S^{j}_{\mu_1 \dots \mu_l}$, $l \neq 0$) will be examined. For the corresponding investigations in the case of spin particles see HESS and WALDMANN[31]. The brackets under consideration are related to the second rank tensor polarization of the molecules in the rotational state j_1 after the collision and essentially determine the saturation values of the field-induced changes $\Delta\eta$ and $\Delta\lambda$ of the viscosity η and the heatconductivity λ of gases of linear rotating molecules (Senftleben-Beenakker effect[4]).

First, consider the Senftleben-Beenakker effect on the viscosity. One finds (cf. MCCOURT and SNIDER[5])

$$-\frac{(\Delta\eta)_{\max}}{\eta_0} = \frac{(\omega_{\eta T})^2}{\omega_\eta \, \omega_T}, \tag{5.3}$$

where η_0 is the isotropic value of the viscosity, while ω_η and ω_T are the relaxation coefficients of the second rank velocity tensor and the second rank tensor in rotational angular momentum (often called "relaxation coefficient of the tensor polarization"), and $\omega_{\eta T}$ is the coupling coefficient between these tensors.

The coupling bracket

$$\begin{aligned}\omega_{\eta T} \propto \sum_{j_1 j_2 j_1' j_2'} \int \exp\left(-\gamma^2 - \mathcal{E}(j_1) - \mathcal{E}(j_2)\right) \gamma^2 \gamma' \\ \cdot \int (\gamma^2 \, \overline{e_\mu \, e_\nu} - \gamma'^2 \, \overline{e_\mu' \, e_\nu'}) \operatorname{tr}_1 \operatorname{tr}_2 \{ a^{j_1 j_2, j_1' j_2'} \\ \cdot (a^\dagger)^{j_1' j_2', j_1 j_2} S^{j_1}_{\mu\nu} \} \, \mathrm{d}^2 e \, \mathrm{d}^2 e' \, \mathrm{d}\gamma\end{aligned} \tag{5.4}$$

is determined by the second rank tensor polarization of the molecules "1" and is of order ε^2 due to the inelastic collisions [cf. (4.18b), (4.21)]. The elastic collisions contribute at least in order ε^3 since, up to the order ε^2, $\operatorname{tr}_1 \operatorname{tr}_2 \{ a^{j_1 j_2, j_1 j_2} (a^\dagger)^{j_1 j_2, j_1 j_2} S^{j_1}_{\mu\nu} \}$ is a symmetric tensor in $\boldsymbol{e}$ and $\boldsymbol{e}'$ in the elastic case and $(\overline{e_\mu \, e_\nu} - \overline{e_\mu' \, e_\nu'})$ is an antisymmetric tensor[31]. The relaxation coefficient of the tensor polarization

$$\begin{aligned}\omega_T \propto \sum_{j_1 j_2 j_1' j_2'} \int \exp\left(-\gamma^2 - \mathcal{E}(j_1) - \mathcal{E}(j_2)\right) \gamma^2 \gamma' \\ \cdot \int \{ \operatorname{tr}_1 \operatorname{tr}_2 | (S^{j_1}_{\mu\nu} + S^{j_2}_{\mu\nu}) \, a^{j_1 j_2, j_1' j_2'} \\ - a^{j_1 j_2, j_1' j_2'} (S^{j_1'}_{\mu\nu} + S^{j_2'}_{\mu\nu}) |^2 \} \, \mathrm{d}^2 e \, \mathrm{d}^2 e' \, \mathrm{d}\gamma\end{aligned} \tag{5.5}$$

is also of order ε^2 because the generalized commutator is of order ε. Thus the effect $\Delta\eta/\eta_0$ is of order ε^2 and mainly determined by the inelastic collisions between the nonspherical molecules. The term in curled brackets, occuring in (5.5) could at least in principle be determined by scattering experiments where two polarized beams are scattered, and where the polarization of the one beam after scattering is detected if one beam is initially polarized.

While for molecules with small nonsphericity the magnitude of the Senftleben-Beenakker effect of the viscosity is mainly determined by the inelastic collisions, the magnitude of the Senftleben-Beenakker effect of the thermal conductivity is mainly due to the elastic collisions[31a]. Here, one has (cf. MCCOURT and SNIDER[5])

$$\frac{(\Delta\lambda)_{\max}}{\lambda_0} \propto \frac{(\omega_{\mathrm{int,\,K}})^2}{\omega_{\mathrm{int}} \cdot \omega_{\mathrm{K}}}, \tag{5.6}$$

where ω_{int} is the relaxation coefficient of the internal energy flux and ω_K is the relaxation coefficient of the "Kagan vector"[31] $\Phi_\mu \propto c_\nu \, S_{\mu\nu}$. The bracket $\omega_{\mathrm{int},\,K}$ couples these two vectors and $\omega_{\mathrm{int},\,K} \propto$

$$\begin{aligned}\sum_{j_1 j_2} \int \exp\left(-\gamma^2 - \mathcal{E}(j_1) - \mathcal{E}(j_2)\right) \left(\mathcal{E}(j_1) - \mathcal{E}(j_2)\right) \gamma^5 \\ \cdot \int (e_\mu - e_\mu') \, e_\nu \{ \operatorname{tr}_1 \operatorname{tr}_2 [a^{j_1 j_2, j_1 j_2} \\ \cdot (a^\dagger)^{j_1 j_2, j_1 j_2} S^{j_1}_{\mu\nu}] \} \, \mathrm{d}^2 e \, \mathrm{d}^2 e' \, \mathrm{d}\gamma + O(\varepsilon^2).\end{aligned} \tag{5.7}$$

Note, that the term linear in ε in (5.7) vanishes for $j_1 = j_2$ (o-H_2 in the rotational ground state). This term linear in ε in (5.7) is due to the elastic collisions while the contributions of $O(\varepsilon^2)$ mainly stem from inelastic collisions. For p-H_2 at room temperature and below, the $2+0 \rightarrow 2+0$ collisions will be the most important ones. Since both relaxation coefficients ω_{int} and ω_K are of order ε^0, the change of thermal conductivity in an applied magnetic field $\Delta\lambda/\lambda_0$ will be proportional to ε^2 as it is true also for the change of the viscosity. This statement allows a comparison to be made of the orders of magnitude[32] for the Senftleben-Beenakker effect of H_2 and HD:

Since in the case of $H_2 - H_2$ the mean nonsphericity parameter is about[1, 33] 0.07 and for HD − HD ε is about 0.3, the ratio $\varepsilon^2_{\mathrm{HD}}/\varepsilon^2_{\mathrm{H_2}}$ is about 20. On the other hand, among the inelastic collisions in p-H_2 the $0+0 \rightarrow 2+0$ and $2+2 \rightleftarrows 2+0$ transitions will be of importance below room tempera-

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[31a] This statement is only true if even Legendre polynomials are dominating in the nonspherical interaction (homonuclear molecules — like H_2, D_2 — possess only even terms) but, in general, not for asymmetric molecules like HD.

[32] The difference of the Senftleben-Beenakker effect for p-H_2 and o-H_2 at low temperatures has been studied theoretically by MAKSIMOV and MIKHAILOVA (cf. Ref. [6]).

[33] Notice, that the parameter ε defined in the present paper is 4/3 times the ε used in Ref. [1].

ture, while in HD the transitions $0+0 \rightarrow 1+0$, $1+0 \rightleftarrows 2+0$, $1+1 \rightleftarrows 2+1$, $0+1 \rightarrow 1+1$ and $2+2 \rightleftarrows 1+2$ will give the dominant contributions. Thus the ratio $(\Delta\eta/\eta_0)^{\mathrm{HD}}_{\mathrm{sat}}/(\Delta\eta/\eta_0)^{\mathrm{p-H_2}}_{\mathrm{sat}}$ may still become larger than 20. These very crude considerations (other differences of the scattering amplitudes and the difference of the reduced masses and the moments of inertia have not been taken into account) are in qualitative agreement with the measurements of KORVING et al.[34] which gave a factor 50 for the ratio of the saturation values of the change of viscosity for HD and p-H_2. For HD and normal H_2 instead of p-H_2 the ratio is still larger, about 150, which may be due to the fact that n-H_2 consists of 3/4 o-H_2 and 1/4 p-H_2 but only ca. 12% of the o-H_2 molecues are in the first excited state $j=3$ at room temperature while ca. 46% of the p-H_2 molecules occupy the first excited state $j=2$. Therefore fewer inelastic collisions will occur in n-H_2 than in p-H_2 gas. Notice, however, that theoretically n-H_2 has to be treated as a gas mixture[35].

The Senftleben-Beenakker effect of p- and o-H_2 will be considered in more detail in a subsequent publication.

Appendix

Some properties of the generalized Legendre functions $P_{ll'L}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})$, defined by Eq. (2.1), will be stated without derivation.

1) The relation between the $P_{ll'L}$ and the Cartesian form of mixed scalar products is:

$$P_{ll'l+l'}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}) = \frac{(2(l+l')-1)!!}{(l+l')!} (l\,0, l'\,0 \,|\, l+l'\,0)^2 \cdot a_{\mu_1} \dots a_{\mu_l}\, b_{\nu_1} \dots b_{\nu_{l'}}\; \overline{c_{\mu_1} \dots c_{\mu_l}\, c_{\nu_1} \dots c_{\nu_{l'}}}\,. \tag{A1}$$

2) Products of ordinary Legendre Polynomials can be written as:

$$P_l(\boldsymbol{a}\cdot\boldsymbol{c})\, P_{l'}(\boldsymbol{b}\cdot\boldsymbol{c}) = \sum_{L=|l-l'|}^{l+l'} P_{ll'L}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})\,. \tag{A2}$$

3) Coupling of two generalized Legendre functions yields:

$$\begin{aligned} P_{ll'L}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})\, P_{kk'K}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}) &= \sum_{\mathrm{pqR}} \sqrt{2L+1}\,\sqrt{2K+1}\,(l\,0, l'\,0 \,|\, L\,0)\,(k\,0, k'\,0 \,|\, K\,0) \\ &\quad \cdot \sqrt{2\mathrm{p}+1}\,\sqrt{2\mathrm{q}+1}\, \frac{(l\,0, k\,0 \,|\, \mathrm{p}\,0)\,(l'\,0, k'\,0 \,|\, \mathrm{q}\,0)\,(L\,0, K\,0 \,|\, \mathrm{R}\,0)}{(\mathrm{p}\,0, \mathrm{q}\,0 \,|\, \mathrm{R}\,0)} \cdot \begin{Bmatrix} l & k & \mathrm{p} \\ l' & k' & \mathrm{q} \\ L & K & \mathrm{R} \end{Bmatrix} P_{\mathrm{pqR}}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})\,, \end{aligned} \tag{A3}$$

where $\begin{Bmatrix} l & k & \mathrm{p} \\ l' & k' & \mathrm{q} \\ L & K & \mathrm{R} \end{Bmatrix}$ is a 9 j-symbol.

4) An orthogonality relation (with respect to $\boldsymbol{c}$) is:

$$\begin{aligned} \int P_{ll'L}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})\, P_{kk'K}(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})\, \mathrm{d}^2 c &= \delta_{LK}(-1)^L \sqrt{2L+1}\,(l\,0, l'\,0 \,|\, L\,0)\,(k\,0, k'\,0 \,|\, K\,0) \\ &\quad \cdot 4\pi \sum_r (-1)^r (l\,0, k\,0 \,|\, r\,0)\,(l'\,0, k'\,0 \,|\, r\,0)\,\sqrt{2r+1} \begin{Bmatrix} l' & k' & r \\ L & L & 0 \\ l & k & r \end{Bmatrix} P_r(\boldsymbol{a}\cdot\boldsymbol{b})\,. \end{aligned} \tag{A4}$$

Finally, some properties of the Cartesian tensor operators $T^{jj'}_{\mu_1 \dots \mu_l}$ which have been defined in § 3 will be listed:

1) The hermitic adjoint of $T^{jj'}_{\mu_1 \dots \mu_l}$ is given by

$$(T^{jj'}_{\mu_1 \dots \mu_l})^\dagger = (-)^{j-j'}\, T^{j'j}_{\mu_1 \dots \mu_l}\,. \tag{A5}$$

2) The orthogonality relation is:

$$\mathrm{tr}\{T^{jj'}_{\mu_1 \dots \mu_l}\,(T^{jj'}_{\nu_1 \dots \nu_l})^\dagger\} = \delta_{ll'}\, \Delta^{(l)}_{\mu_1 \dots \mu_l,\, \nu_1 \dots \nu_l}\,. \tag{A6}$$

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[34] J. KORVING, H. HULSMAN, G. SCOLES, H. F. P. KNAAP, and J. J. M. BEENAKKER, Physica **36**, 177 [1967].

[35] H. H. RAUM and W. E. KÖHLER, Z. Naturforsch. (to be published).

3) For $l \leqq 2$ the following trace formulas for triple products of T-tensors hold:

$$\mathrm{tr}\{T_{\mu}^{jj'}\, T_{\nu}^{j'j}\, T_{\varkappa\lambda}^{jj}\} = 3\, W(j\,j\,1\,1;2\,j')\, \Delta_{\mu\nu,\,\varkappa\lambda}\,, \tag{A7}$$

and

$$\mathrm{tr}\{T_{\mu\nu}^{jj'}\, T_{\varkappa\lambda}^{j'j}\, T_{\sigma\tau}^{jj}\} = -10\sqrt{\tfrac{3}{7}}\, W(j\,j\,2\,2;2\,j')\, \Delta_{\mu\nu,\,\mu'\nu'}\, \Delta_{\varkappa\lambda,\,\mu'\lambda'}\, \Delta_{\sigma\tau,\,\nu'\lambda'}\,, \tag{A8}$$

where $W(j\,j\,1\,1;2\,j')$ and $W(j\,j\,2\,2;2\,j')$ are Racah coefficients. Formula (A8) together with the explicit expression for $W(j\,j\,2\,2;2\,j+2)$ has been used for deriving Eq. (4.19b).

Spectrum of the Depolarized Rayleigh Light Scattered by Gases of Linear Molecules

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The spectrum of the depolarized Rayleigh light scattered by a gas of linear molecules is calculated by a kinetic theory approach based on the Waldman-Snider equation. Collisional and diffusional broadening are studied. The line width is related to relaxation coefficients which are collision brackets obtained from the linearized Waldmann-Snider collision term involving the binary molecular scattering amplitude and its adjoint. It is shown under which conditions the relaxation coefficients characterizing the line width can be compared with data obtained from Sentfleben-Beenakker effect and nuclear magnetic relaxation measurements.

The "depolarized Rayleigh" component[1] of the light scattered by a gas of linear molecules is associated with fluctuations of the (2nd rank) tensor polarization of the rotational angular momentum of the molecules and, in particular, its spectrum is determined by the spectral function of the tensor polarization[2, 3]. The spectrum of the depolarized Rayleigh light has resently been measured[4] for some gases of linear molecules (H_2, N_2, CO_2) in the pressure region where the width of the line is primarily caused by collisional broadening (pressure broadening). In this paper, the spectrum of the depolarized Rayleigh ligth is calculated by a kinetic theory approach based on the Waldmann-Snider equation[5]. Both collisional and diffusional broadening are studied.

Collisional broadening of the depolarized Rayleigh scattering has been treated theoretically by GORDON[6] who developed a classical theory which is akin to Anderson's impact theory[7] for the pressure broadening of absorption and emission spectra.

By the kinetic equation approach used in this paper the calculation of the spectrum of the light scattered by a gas is based on the same generalized Boltzmann equation (Waldmann-Snider equation) as the calculation of transport properties of polyatomic gases. The line width is expressed in terms of collision brackets obtained from the linearized Waldmann-Snider collision term which involves the binary scattering amplitude operator and its adjoint. Thus a rigorous connection between the line width and the molecular (binary) collision processes is established. Furthermore it is possible to obtain relations between line widths and transport properties since transport coefficients can also be expressed in terms of collision brackets.

This paper proceeds as follows: Firstly, after some preliminary remarks on the one-particle distribution function operator for a gas of linear molecules and the definition of the second rank tensor polarization, the connection between the spectrum of the depolarized Rayleigh light and the spectral

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[1] "Depolarized" refers to the component of the scattered light whose electric field vector is perpendicular to the electric field of the linearly polarized incident light. "Rayleigh" refers to the line of the spectrum of the scattered light which is centered at the frequency of the incident (monochromatic) light. Some of the results derived in this paper have been reported earlier, cf. S. HESS, Z. Naturforsch. **24 a**, 1852 [1969].

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