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 H₂ and HD.

In a previous paper 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 (bulk viscosity), for the influence of magnetic and electric fields on the heat conductivity and viscosity (Senftleben-Beenakker effects), for flow birefringence and the electric polarization caused by a temperature gradient, for nuclear spin relaxation, for depolarized Rayleigh light scattering, and for rotational Raman scattering. Using an approach based on the quantum mechanical kinetic equation 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 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 $\text{H}_2$ 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 $\text{H}_2$ 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 $\mathcal{J}$ matrix which, in turn, is related to the interaction potential by the Lippmann-Schwinger equation. Then the nonsphericity parameter $\epsilon$ which, in essence, measures the ratio of the nonspherical and spherical parts of the interaction potential, is introduced. Assuming that $\epsilon$ is small (small nonsphericity) one can expand the $\mathcal{J}$ matrix with respect to this parameter (§1). The dependence of the nonspherical $\mathcal{J}$ operator (and consequently of the scattering amplitude operator) in order $\epsilon$ 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 $\epsilon$ in a rather simple way. As specific examples, the hydrogen molecules $\text{H}_2$ and $\text{HD}$ 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 $\text{H}_2$ and $\text{HD}$ (§5).

§1. Scattering Amplitude in the Approximation of Small Nonsphericity

The scattering amplitude operator $a(\mathbf{k}, \mathbf{k}')$ is linked with the binary scattering $\mathcal{J}$ operator in the center of mass system by

$$a(\mathbf{k}, \mathbf{k'}) = -\frac{m_{12}}{2\pi\hbar^2} \langle \mathbf{k} | \mathcal{J} | \mathbf{k}' \rangle,$$  

(1.1)

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

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

$$\mathcal{J} = \mathcal{V} + \mathcal{V}G_0^{(+)} \mathcal{J},$$  

(1.2)

and the "formal solution" of (1.2) is

$$\mathcal{J} = \mathcal{V} + \mathcal{V}G^{(+)}\mathcal{V},$$  

(1.3)

where $G^{(+)} = (E - H + i\eta)^{-1}$ 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 $\mathbf{x}$ 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

$$\mathcal{V} = V + \epsilon v,$$  

(1.4)

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

The expansion of (1.3) in powers of $\varepsilon$ (cf. Ref.1) yields

$$\mathcal{T} = T^{(0)} + \varepsilon T^{(1)} + \varepsilon^2 T^{(2)} + \ldots$$

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

$$T^{(0)} = V(1 + G^{(+)} V),$$

$$T^{(1)} = (1 + V G^{(+)} v(1 + G^{(+)} V),$$

$$T^{(2)} = (1 + V G^{(+)} v G^{(+)} v (1 + G^{(+)} V).$$

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 $\varepsilon$ 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 $|jm\rangle$. The projection operator into the $j$-subspace can now be defined by

$$P_j = \sum_m |jm\rangle\langle jm|.$$ (1.7)

The corresponding two particle projection operator is then

$$P_{j1j2} = P_{j1} \otimes P_{j2},$$

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

$$a_{j1j2}^{j'1j'2} = P_{j1j2} a_{j1j2},$$

and the total scattering amplitude operator $a$ is then

$$a = \sum_{j1j2} a_{j1j2}^{j1j2},$$

since $\sum_{j1j2} P_{j1j2} = 1$.

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

$$a_{j1j2}^{j1j2} (k, k') = - \frac{m_{12}}{2\pi \hbar^2} \langle k | T^{(0)} | k' \rangle$$

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 $k$ and $k'$ occurring in (1.11) are connected by

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

with $E(j) = \hbar^2 j(j + 1)/2 \Theta$ and $\Theta$ 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

$$\frac{1}{(2 j_1'+1)(2 j_2'+1) k'}\text{tr}_1 \text{tr}_2 \{a_{j1j2}^{j1j2} (a^\dagger)^{j'1j'2} (a^\dagger)^{j1j2} \}.$$ (1.13)

It is of order $\varepsilon^0$ for energetically elastic encounters and of order $\varepsilon^2$ 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 $\text{HD} - \text{HD}$. The expansion
of the intermolecular potential in terms of polynomials which take into account the relative orientations of the molecular axes $\mathbf{u}^{(1)}$ and $\mathbf{u}^{(2)}$ (unit vectors) and the unit vector $\mathbf{x}$ 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 $P_{\ell'\ell}^{[i]}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x})$ of the three unit vectors $\mathbf{u}^{(1)}$, $\mathbf{u}^{(2)}$, and $\mathbf{x}$.

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

$$V_{\ell'\ell}^{[i]}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x}) = \sum_{\ell''} P_{\ell''}^{[\ell']}(\mathbf{b}) \cdot Y_{\ell''m''}(\mathbf{c}) \cdot \sum_{\ell'''} V_{\ell''m''}^{[\ell''']} (\mathbf{a}) \cdot Y_{\ell'''m'''}(\mathbf{c}) \cdot \delta_{\ell''\ell'''} \cdot \delta_{m''m'''},$$

(2.1)

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

$$P_{000}(\mathbf{a}, \mathbf{b}, \mathbf{c}) = 1,$$

(2.2a)

$$P_{0l0}(\mathbf{a}, \mathbf{b}, \mathbf{c}) = P_l(\mathbf{a} \cdot \mathbf{c}) \delta_{\ell l},$$

(2.2b)

$$P_{0l'0}(\mathbf{a}, \mathbf{b}, \mathbf{c}) = (2l + 1)^{-1} P_l(\mathbf{a} \cdot \mathbf{c}) \delta_{l l'},$$

(2.2c)

$$P_{l00}(\mathbf{a}, \mathbf{b}, \mathbf{c}) = (2l + 1)^{-1} P_l(\mathbf{a} \cdot \mathbf{c}) \delta_{l l'}.$$  

(2.2d)

The expansion of the nonspherical interaction potential $V$ can be written as

$$V(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x}) = \sum_{\ell'\ell} V_{\ell'\ell}(r) P_{\ell'\ell}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x}).$$

(2.3)

The functions $V_{\ell'\ell}(r)$ may be decomposed into a sum of a repulsive short range part $V_{\ell'\ell}^{(r)}(r)$ and an attractive long range part $V_{\ell'\ell}^{(a)}(r)$. Little information is available regarding the short range part except in the case of the $\text{H}_2-\text{He}$ interaction where ab initio calculations have been performed by Roberts et al. 18

$$V_{\text{disp}}^{\text{disp}}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x}) = -A \alpha_1 \alpha_2 r^{-6} \left[ 1 + \frac{1}{3} \gamma^{(1)} P_2(\mathbf{u}^{(1)} \cdot \mathbf{x}) \right] + \frac{1}{3} \gamma^{(2)} P_2(\mathbf{u}^{(2)} \cdot \mathbf{x}) + \frac{1}{3} \gamma^{(1)} \gamma^{(2)} P_{222}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x}) + \frac{1}{3} \gamma^{(1)} \gamma^{(2)} P_{222}(\mathbf{u}^{(2)}, \mathbf{u}^{(1)}, \mathbf{x}) \right],$$

(2.6a)

or, written in Cartesian notation,

$$V_{\text{disp}}^{\text{disp}}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x}) = -A \alpha_1 \alpha_2 r^{-6} \left[ 1 + \frac{1}{3} \sum_{\mu=0}^{\infty} u_\mu^{(1)} u_\mu^{(1)} \right] + \frac{1}{3} \sum_{\mu=0}^{\infty} u_\mu^{(2)} u_\mu^{(2)} + \frac{1}{3} \sum_{\mu=0}^{\infty} u_\mu^{(1)} u_\mu^{(2)} + \frac{1}{3} \sum_{\mu=0}^{\infty} u_\mu^{(2)} u_\mu^{(1)} \right].$$

(2.6b)

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

$$\frac{\alpha^{(i)}}{\alpha^{(0)}},$$

20 Cartesian indices are denoted by Greek subscripts, the summation convention is used and the symbol $\rightarrow$ refers to the irreducible (symmetric traceless) part of a tensor, e. g. $a_{\mu b} = \frac{1}{2} (a_{\mu} b_{\nu} + b_{\mu} a_{\nu}) - \frac{1}{2} \mathbf{a} \cdot \mathbf{b} \delta_{\mu \nu}.$
21 Note, that the $P_{\ell'\ell}^{[i]}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x})$ are functions of the three angles $\chi_1, \chi_2, \varphi$ of Ref. 1, if $\mathbf{x}$ is taken as polar axis.
31a Note, that the vector $\mathbf{x}$ 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 H₂, y is about 22° so that terms containing products yd) y( 2) jn (2.6 a, b) may, in first approximation, be neglected compared with those linear in y₀. The induction energy V⁻ for molecules with dipole moments \( \mathbf{d}_1 = d_1 \mathbf{u}^{(1)} \), \( \mathbf{d}_2 = d_2 \mathbf{u}^{(2)} \) is given (to lowest order in the polarizabilities) by

\[
V_{\text{ind}}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x}) = -\alpha d_1^2 r^{-6} [1 + P_2(u^{(1)}_\mathbf{u} \cdot \hat{x}) + y^{(1)}(\frac{1}{2} P_2(u^{(1)}_\mathbf{u} \cdot \hat{x})) + 2P_{224}(u^{(1)}_\mathbf{u}, u^{(2)}_\mathbf{u}, \hat{x}) + \frac{1}{15} P_2(u^{(1)}_\mathbf{u} \cdot u^{(2)}_\mathbf{u}) - \frac{1}{15} P_{222}(u^{(1)}_\mathbf{u}, u^{(2)}_\mathbf{u}, \hat{x})] + (1, 2) \text{ interchanged}. \tag{2.7}
\]

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

\[
V_{\text{elec}} = V_{\text{d.d}} + V_{\text{d.q}} + V_{\text{q-q}} + \text{higher order multipole terms.}
\]

The dipole-dipole interaction is

\[
V_{\text{d.d}}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x}) = -3 d_1 d_2 r^{-3} u^{(1)}_\mathbf{u} u^{(2)}_\mathbf{u} \frac{\hat{x}_1 \hat{x}_2}{\mathbf{x}_1 \cdot \mathbf{x}_2} = -3 d_1 d_2 r^{-3} P_{112}(u^{(1)}_\mathbf{u}, u^{(2)}_\mathbf{u}, \hat{x}), \tag{2.8}
\]

the dipole-quadrupole terms are

\[
V_{\text{d.q}}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x}) = -\frac{4}{5} r^{-4} d_1 Q_1 u^{(1)}_\mathbf{u} u^{(2)}_\mathbf{u} \frac{\hat{x}_1 \hat{x}_2}{\mathbf{x}_1 \cdot \mathbf{x}_2} - (1, 2) \text{ interchanged}
\]

\[
= 5 r^{-4} d_2 Q_1 P_{123}(u^{(1)}_\mathbf{u}, u^{(2)}_\mathbf{u}, \hat{x}) - (1, 2) \text{ interchanged,} \tag{2.9a}
\]

and the quadrupole-quadrupole interaction is

\[
V_{\text{q-q}}(\mathbf{u}^{(1)}, \mathbf{u}^{(2)}, \mathbf{x}) = \frac{10}{3} Q_1 Q_2 r^{-5} u^{(1)}_\mathbf{u} u^{(2)}_\mathbf{u} \frac{\hat{x}_1 \hat{x}_2}{\mathbf{x}_1 \cdot \mathbf{x}_2} = \frac{1}{15} Q_1 Q_2 r^{-5} P_{224}(u^{(1)}_\mathbf{u}, u^{(2)}_\mathbf{u}, \hat{x}). \tag{2.9b}
\]

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, / and \( y^{(2)} \) are equal to zero. This implies, that only ordinary Legendre polynomials \( P_i(u^{(1)}_\mathbf{u} \cdot \hat{x}) \) occur.

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

\[
V(u^{(1)}_\mathbf{u}, u^{(2)}_\mathbf{u}, \mathbf{x}) = V(r) + \sum_L \sum_{(l, l')} \sum_{\epsilon \notin l, l'} U_{ll'}(r) P_{ \epsilon l}(u^{(1)}_\mathbf{u}, u^{(2)}_\mathbf{u}, \hat{x}), \tag{2.10}
\]

where the \( U_{ll'}(r) \) are of the same order of magnitude as \( V(r) = V_{000}(r) \). The \( \epsilon \notin l, l' \) are the nonsphericity parameters belonging to the corresponding generalized Legendre functions. In certain important cases (H₂, D₂, HD) it may be sufficient to take into account only one nonzero value for \( l \) and \( l' \).

As examples the hydrogen molecules H₂ and HD are considered. For the H₂—H₂ 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 H₂—H₂ interaction has the form

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

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, Takayanagi and Niblett, and the mean nonsphericity parameter \( \varepsilon \) is about 0.07.

In calculations with HD a modified Morse potential has been used by Takayanagi and Sluijter and Takayanagi calculated the rotational relaxation coefficient for the \( 0 + 0 \rightarrow 1 + 0 \) transition in HD. This ad hoc potential had the form

\[
V(u^{(1)}_\mathbf{u}, \mathbf{x}) = V(r) + \varepsilon v_{10}(r) P_1(u^{(1)}_\mathbf{u} \cdot \hat{x}), \tag{2.12}
\]

\[26\] The interaction potential for HD—HD is assumed to be the same as for H₂—H₂ if it is expressed as function of the vector connecting the geometrical midpoints of the molecules. Rewriting the H₂—H₂ 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

\[ V(r) = D \left\{ \exp\left[ -2 \alpha (r - r_0) \right] - 2 \exp\left[ -\alpha (r - r_0) \right] \right\}, \]

(2.13a)

and

\[ \epsilon v_{10}(r) = D \left\{ \beta_1 \exp\left[ -2 \alpha (r - r_0) \right] - \beta_2 \exp\left[ -\alpha (r - r_0) \right] \right\}. \]

(2.13b)

Higher order Legendre polynomials have been neglected. The constants \( D, r_0, \alpha, \beta_1, \beta_2 \) 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 \( P_1(u^{(1)} \cdot \hat{x}) \) by the symmetrized term \([P_1(u^{(1)} \cdot \hat{x}) - P_1(u^{(2)} \cdot \hat{x})] \) where the minus sign appears because \( \hat{x} = \hat{x}_{12} = -\hat{x}_{21} \).

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 \( r < 4 a_0 \) (\( a_0 \) is the Bohr radius) it is about 0.45 and for \( r > 8 a_0 \) it is about 0.21. A mean nonsphericity parameter may thus be given by \( \epsilon \approx 0.3 \). 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 \( \epsilon^2 \) in the scattering \( T \) matrix could give a non-negligible contribution so that a first order DWBA calculation may not be sufficient, except for order-of-magnitude considerations.

§ 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

\[ T^{jj'}_{lm} = \sum_{m'} (-1)^{l-m'} (j' m', j - m' | lm) |jm'| \langle j' m' |, \]

(3.1)

one has

\[ [Y^*_{lm}(u)]^{j''}_{j'\prime} = P^j_{j''} \delta^{j'' j'} \delta^{l' l''} + \sum_L \sum_{(j, l', j', l'')} \epsilon_{l'' l'} U_{l'' L}(r) P^{j''}_{j' \prime} D^{jj''}_{L} T^{jj''}_{lm} Y_{LM}(\hat{x}). \]

(3.3)

with the scalar two particle operator

\[ P^{jj'}_{j'\prime} D^{jj''}_{L} = (4 \pi)^{1/2} \sqrt{\frac{(2j+1)(2j'+1)}{(2L+1)(2L'+1)}} \sum_{m, m', M} (L m, l' m' | L M) T^{jj''}_{lm} T^{jj'}_{j'\prime m} Y_{LM}(\hat{x}). \]

(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 \( T \) matrix linear in \( \epsilon \), 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 \( T^{jj'}_{\mu \mu', \mu'} \), defined by the equality of scalar products in spherical and Cartesian form

\[ \sqrt{4 \pi} \sum_m T^{jj'}_{lm} Y_{lm}(\hat{x}) = \sqrt{\frac{(2L+1) !}{l!}} T^{jj'}_{\mu \mu', \mu'} \hat{x}_{\mu} \cdots \hat{x}_{\mu'}. \]

(3.5)

Here, in analogy with (3.2), the operator form of the tensor \( u_{\mu_1} \cdots u_{\mu_l} \) is

\[ u_{\mu_1} \cdots u_{\mu_l} |^{jj'}_{jj'} \]

(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 \( T^{jj'}_{\mu_1 \cdots \mu_l} \) is related to the well known hermitian tensor operator for spin \( j \), \( P^j_{j_1 \cdots j_\mu} \cdots J_{\mu} \), which is built up from the vector spin operators \( J_{\mu} \) (with \( J_{\mu} = J_{\mu} \), \( J_{\mu} = i \epsilon_{\mu \nu \lambda} J_{\lambda} \) by
\[ T_{\mu_1 \cdots \mu_l}^{\mu_1' \cdots \mu_{l'}} = p I j_{\mu_1} \cdots j_{\mu_l} p I^l \left[ (2l+1)!! \right]^{1/2} \frac{1}{2^l j_1+1} (j_{(0)} \cdots j_{(l-1)})^{-1}, \]  
with 
\[ j_{(0)} = \sqrt{j(j+1) - \frac{1}{2} l \left( \frac{1}{2} l + 1 \right)}. \]

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 \( \text{H}_2, \text{HD} \) 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
\[ v(u^{(1)}, u^{(2)}, x) = \epsilon v_{(0)}(r) [P_I(u^{(1)} \cdot \hat{x}) + (-)^l P_I(u^{(2)} \cdot \hat{x})] \]
\[ = \epsilon v_{(0)}(r) \left[ (2l-1)!! \frac{1}{l!} \sum_{m_1 \cdots m_l} (u^{(1)}_{m_1} \cdots u^{(1)}_{m_l}) (u^{(2)}_{m_1} \cdots u^{(2)}_{m_l}) + (-)^l (u^{(2)}_{m_1} \cdots u^{(2)}_{m_l}) \right] \]  
(3.9)

[the factor \((-)^l \) is necessary, because \( \hat{x} \equiv \hat{x}_{12} = -\hat{x}_{21} \) and the potential must be symmetric with respect to an interchange of 1 and 2] the scattering amplitude is, to terms linear in \( \epsilon \)
\[ a = a_{\text{sph}} + \epsilon \sum a_{\text{nonsph}}^{j_1j_2j_1'j_2'}. \]  
(3.10)

A matrix element of \( a_{\text{nonsph}}^{j_1j_2j_1'j_2'} \) can be obtained from (1.1) and (1.6b):
\[ (a_{\text{nonsph}}^{j_1j_2j_1'j_2'})_{m_1m_1'am_2m_2'} = \frac{-m_{12}}{2 \pi \hbar^2} (2l-1)!! \left[ \langle k, j_1 m_1, j_2 m_2 \mid [1 + V(E - H_{\text{int}} - K - V + i \eta)]^{-1} \right] \]
\[ \langle k', j_1' m_1', j_2' m_2' \rangle \]  
(3.11)

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

Since
\[ H_{\text{int}} | j_1 m_1, j_2 m_2 \rangle = (E(j_1) + E(j_2)) | j_1 m_1, j_2 m_2 \rangle, \]  
(3.12)

and
\[ E - E(j_1) - E(j_2) = \frac{\hbar^2 k^2}{2 m_{12}}, \quad E - E(j_1') - E(j_2') = \frac{\hbar^2 k'^2}{2 m_{12}} \]  
(3.13)

and \( V, K, \) and \( v_{(0)} \) do not act on internal states, Eq. (3.11) can be rewritten in the form
\[ (a_{\text{nonsph}}^{j_1j_2j_1'j_2'})_{m_1m_1'am_2m_2'} = \left( \frac{2l-1} {l!} \right) A_{\mu_1 \cdots \mu_l}(k, k') \left\{ \langle j_1 m_1 | \frac{1}{u^{(1)}_{m_1} \cdots u^{(1)}_{m_l}} | j_1' m_1' \rangle \delta_{j_1j_1'} \delta_{m_1m_1'} \right. \]
\[ + (-)^l \left( j_2 m_2 | \frac{1}{u^{(2)}_{m_1} \cdots u^{(2)}_{m_l}} | j_2' m_2' \rangle \delta_{j_2j_2'} \delta_{m_2m_2'} \right) \} \]  
(3.14)

In Eq. (3.14) the \( l \)-th rank tensor \( A_{\mu_1 \cdots \mu_l}(k, k') \) is given by
\[ A_{\mu_1 \cdots \mu_l}(k, k') = \frac{-m_{12}}{2 \pi \hbar^2} \langle \chi_k^{(-)} | v_{(0)} \sum_{m_1} \frac{\hat{x}_{m_1} \cdots \hat{x}_{m_l}}{u^{(1)}_{m_1} \cdots u^{(1)}_{m_l}} | \chi_{k'}^{(+)}) \rangle \]  
(3.15)

where the states
\[ | \chi_k^{(\pm)} \rangle = \left[ 1 + \left( \frac{\hbar^2 k^2}{2 m_{12}} - K - V \pm i \eta \right)^{-1} V \right] | k \rangle \]  
(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
\[ a_{\text{nonsph}}^{j_1j_2j_1'j_2'}(k, k') = \sqrt{\left( \frac{2l-1} {l!} \right) \frac{1}{(2l+1)!} A_{\mu_1 \cdots \mu_l}(k, k')} \]
\[ \cdot \{ 2^{1/2} j_1 + 1 (j_1 0, l 0 | j_1' 0) T_{\mu_1 \mu_1'}^{j_1j_1'} \delta_{j_2j_2'} P^h + (-)^l 2^{1/2} j_2 + 1 (j_2 0, l 0 | j_2' 0) T_{\mu_2 \mu_2'}^{j_2j_2'} \delta_{j_1j_1'} P^h \} \]  
(3.17)

On the energy shell the magnitudes of \( k \) and \( k' \) are connected by Eq. (1.12).
The tensor \( A_{\mu_1...\mu_l}(k, k') \) can be expanded into a sum of the \((l+1)\) irreducible \(l\)-th rank tensors which can be constructed from the unit vectors \( \mathbf{e} \) and \( \mathbf{e}' \):

\[
A_{\mu_1...\mu_l}(k, k') = a_0(k, k', \mathbf{e} \cdot \mathbf{e'}) e_{\mu_1} ... e_{\mu_l} + a_1(k, k', \mathbf{e} \cdot \mathbf{e'}) e'_{\mu_1} e_{\mu_2} ... e_{\mu_l} + \ldots + a_{l-1}(k, k', \mathbf{e} \cdot \mathbf{e'}) e_{\mu_1} e_{\mu_2} ... e_{\mu_l} + a_l(k, k', \mathbf{e} \cdot \mathbf{e'}) e'_{\mu_1} e'_{\mu_2} ... e'_{\mu_l}.
\]

(3.18)

The angle of deflection \( \theta \) is defined by \( \cos \theta = \mathbf{e} \cdot \mathbf{e}' \) (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 \( \mathbf{J} \) and the Cartesian unit vector \( \mathbf{u} \) are used for the description of intramolecular mechanics. The vector \( \mathbf{u} \) is restricted by the constraints

\[
\mathbf{u} \cdot \mathbf{u} = 1, \quad \mathbf{u} \cdot \mathbf{J} = 0.
\]

(3.19)

Thus, it has only one free component which together with \( \mathbf{J} \) gives four independent variables equivalent to the canonical set \( \theta, \varphi, p_\theta, p_\varphi \) of the internal spherical coordinates of the rotator. According to the physical meaning of \( \mathbf{J} \) as the operator of infinitesimal rotation, its commutator with \( \mathbf{u} \) is

\[
[J_\mu, u_\nu] = i \epsilon_{\mu\nu\lambda} u_\lambda.
\]

(3.20)

The constraints (3.19) are compatible with (3.20). The same commutation rule is valid for \( \mathbf{J} \) itself,

\[
[J_j, J_k] = \pm i \epsilon_{jkl} J_l; \quad [u_\mu, u_\nu] = 0.
\]

Now, these commutation rules are invariant under "time reversal", i.e. under replacing \( \mathbf{J}, \mathbf{u} \) by \( -\mathbf{J}, -\mathbf{u} \). 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):

\[
a(E, \mathbf{e}, \mathbf{e}', \mathbf{J}_1, \mathbf{u}_1, \mathbf{J}_2, \mathbf{u}_2) = a(E, -\mathbf{e}', -\mathbf{e}, -\mathbf{J}_1, -\mathbf{u}_1, -\mathbf{J}_2, -\mathbf{u}_2).
\]

(3.21)

This is the general expression of the time reversal invariance.

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

\[
a_{\text{nonph}}(E, \mathbf{e}, \mathbf{e}', \mathbf{J}_1, \mathbf{u}_1, \mathbf{J}_2, \mathbf{u}_2) = \frac{(2l-1)!!}{l!} \sum_{j_1} \sum_{j_2} \sum_{h_1} \sum_{h_2} \sum_{i_1} \sum_{i_2} \sum_{j_1'} \sum_{j_2'} \sum_{h_1'} \sum_{h_2'} \sum_{i_1'} \sum_{i_2'} \sum_{j_1''} \sum_{j_2''} \sum_{h_1''} \sum_{h_2''} \sum_{i_1''} \sum_{i_2''} \sum_{j_1'''} \sum_{j_2'''}) \left( K_{h_1, h_2}, K_{j_1, j_2} \right) \left( K_{h_1', h_2'}, K_{j_1', j_2'} \right) \left( K_{h_1'', h_2''} \right) \left( K_{j_1'', j_2''} \right).
\]

Here

\[
K_{h, j} = E - E(j_1) - E(j_2), \quad K_{j, j'} = E - E(j_1') - E(j_2').
\]

The relative kinetic energies. The time reversal operation yields

\[
a_{\text{nonph}}(E, -\mathbf{e}'', -\mathbf{e}, -\mathbf{J}_1, -\mathbf{u}_1, -\mathbf{J}_2, -\mathbf{u}_2) = \frac{(2l-1)!!}{l!} \sum_{j_1} \sum_{j_2} \sum_{h_1} \sum_{h_2} \sum_{i_1} \sum_{i_2} \sum_{j_1'} \sum_{j_2'} \sum_{h_1'} \sum_{h_2'} \sum_{i_1'} \sum_{i_2'} \sum_{j_1''} \sum_{j_2''} \sum_{h_1''} \sum_{h_2''} \sum_{i_1''} \sum_{i_2''} \sum_{j_1'''} \sum_{j_2'''}) \left( K_{h_1, h_2}, K_{j_1, j_2} \right) \left( K_{h_1', h_2'}, K_{j_1', j_2'} \right) \left( K_{h_1'', h_2''} \right) \left( K_{j_1'', j_2''} \right).
\]

or, by renaming the indices \( j_1 \ldots j_2' \):

\[
a_{\text{nonph}}(E, -\mathbf{e}'', -\mathbf{e}, -\mathbf{J}_1, -\mathbf{u}_1, -\mathbf{J}_2, -\mathbf{u}_2) = \frac{(2l-1)!!}{l!} \sum_{j_1} \sum_{j_2} \sum_{h_1} \sum_{h_2} \sum_{i_1} \sum_{i_2} \sum_{j_1'} \sum_{j_2'} \sum_{h_1'} \sum_{h_2'} \sum_{i_1'} \sum_{i_2'} \sum_{j_1''} \sum_{j_2''} \sum_{h_1''} \sum_{h_2''} \sum_{i_1''} \sum_{i_2''} \sum_{j_1'''} \sum_{j_2'''}) \left( K_{h_1, h_2}, K_{j_1, j_2} \right) \left( K_{j_1', j_2'} \right) \left( K_{j_1'', j_2''} \right).
\]

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

\[
A_{\mu_1...\mu_l}(K_{j_1, j_2}, K_{j_1', j_2'}, \mathbf{e}, \mathbf{e}') = A_{\mu_1...\mu_l}(K_{j_1'', j_2''}, \mathbf{e}, \mathbf{e'}).
\]

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

$$
\sum_{i=0}^{L} a_i(K_{h, i}, K_{h', i'}, \theta) \left( (e^{I-i} e^{I})^\dagger \right)_{\mu_1 \ldots \mu_L} = \sum_{i} a_i(K_{h, i}, K_{h', i'}, \theta) \left( (e^{-I-i} e^{-I}) \right)_{\mu_1 \ldots \mu_L} = \left( -1 \right)^L \sum_{i} a_{L-i}(K_{h, i'}, K_{h', i}, \theta) \left( (e^{I-i} e^{I}) \right)_{\mu_1 \ldots \mu_L},
$$
or, term by term

$$
a_i(K_{h, i}, K_{h', i'}, \theta) = \left( -1 \right)^i a_{L-i}(K_{h, i'}, K_{h', i}, \theta).
$$

(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 $J, \mathbf{u}$ by $\mathbf{u}, -J$ and, for the translational motion, replacing $\mathbf{x}, \mathbf{p}$ by $-\mathbf{x}, -\mathbf{p}$. Again, from reflection invariance of the total Hamiltonian follows

$$
a(E, \mathbf{e}, e^\prime, \mathbf{J}_1, u_1, \mathbf{J}_2, u_2) = a(-E, \mathbf{e}, -e^\prime, \mathbf{J}_1, -u_1, \mathbf{J}_2, -u_2) \quad (3.24)
$$

Considering the examples $\text{H}_2(D_2^2)$ and HD, the following results can be stated:

1) For $\text{H}_2 - \text{H}_2$ the $l=2$ term in the nonspherical interaction potential is the most important one, so that $j_1 = j_1', j_2 = j_2'$ and $(1, 2)$ interchanged. Then the total scattering amplitude is

$$
a = a_{\text{sp}} + \frac{\epsilon}{V^1 \mathbf{j}} \left\{ \sum_{j_1, j_2} \left[ -A^{(0)}_{\mu\nu} \sqrt{\frac{\mathbf{j} + 1}{2 \mathbf{j} + 1}} \mathbf{A}_{\mu j_1} + A^{(2)}_{\mu j_1} \sqrt{\frac{3(\mathbf{j} + 2)(\mathbf{j} + 3)}{2(\mathbf{j} + 1)}} \mathbf{T}_{\mu j_1} \right] \right\},
$$

(3.25)

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

$$
A^{(\alpha)}_{\mu\nu} = A^{(\alpha)}_{\mu\nu} - A^{(\alpha)}_{\mu\nu} \quad \text{with}
$$

(3.26a)

and with $k^{(0)} = k$ and $a^{(0)}_{\mu\nu} = a^{(0)}_{\mu\nu}$ (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

$$
a = a_{\text{sp}} - \frac{\epsilon}{V^3} \left\{ \sum_{j_1, j_2} \left[ A^{(1)}_{\mu j_1 + 1} \mathbf{T}^{(1)}_{\mu j_1} - A^{(1)}_{\mu j_1 - 1} \mathbf{T}^{(1)}_{\mu j_1} \right] \right\}.
$$

(3.27)

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

$$
A^{(\alpha)}_{\mu} = a^{(\alpha)}_{\mu} e^\mu + a^{(\alpha)}_{\mu} e^\mu.
$$

(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.


a) Description of a polarized beam

Consider a beam of molecules in a specific rotational state \( j \). It is described by a density matrix \( \varrho^j \). 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 occurrence 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 \( l_{\text{max}} = 2j \). 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

\[
\langle S^j_{\mu_1 \ldots \mu_l} \rangle = \text{tr} \{ \varrho^j S^j_{\mu_1 \ldots \mu_l} \},
\]

where, for convenience, the operators

\[
S^j_{\mu_1 \ldots \mu_l} = \sqrt{2j + 1} T^j_{\mu_1 \ldots \mu_l},
\]

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

\[
\text{tr} \{ S^j_{\mu_1 \ldots \mu_l} S^j_{\nu_1 \ldots \nu_l} \} = (2j + 1)(2j + 1).
\]

This result is a consequence of the trace property

\[
\text{tr} \{ S^j_{\mu_1 \ldots \mu_l} S^j_{\nu_1 \ldots \nu_l} \} = (2j + 1) \delta_{ll'} A^{(l)}_{\mu_1 \mu_2 \ldots \mu_l \nu_1 \nu_2 \ldots \nu_{l'},}
\]

where \( A^{(l)}_{\mu_1 \mu_2 \ldots \mu_l \nu_1 \nu_2 \ldots \nu_{l'}} \) is an isotropic tensor which, when applied to an arbitrary \( l \)-th rank tensor, projects out the symmetric irreducible part of that tensor. For properties of the \( A^{(l)}_{\mu_1 \mu_2 \ldots \mu_l \nu_1 \nu_2 \ldots \nu_{l'}} \) 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:

\[
S^j_{\mu} = 3(2j + 1)^{-1/2} p^j \mathbf{J}_\mu p^j ,
\]

\[
S^j_{\mu
u} = \sqrt{\frac{15}{2}} \{ j(j+1) \}^{-1/2} p^j \mathbf{J}_\mu \mathbf{J}_\nu p^j .
\]

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

\[
\varrho^j = (2j + 1)^{-1} \{ p^j + \langle S^j_0 \rangle S^j_0 \} + \cdots + \langle S^j_{\mu_1 \ldots \mu_2} \rangle S^j_{\mu_1 \ldots \mu_2} .
\]

b) Observables 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 \( \varrho_{\text{in}} \). The density operator \( \varrho_{\text{fin}} \), describing the molecules after the collision is related to \( \varrho_{\text{in}} \) by

\[
\varrho_{\text{fin}} = a \varrho_{\text{in}} a^*,
\]

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 beam of molecules in the rotational state \( j'_2 \) is considered. The density matrix for the final state is

\[
\varrho_{\text{fin}} = \varrho_{\text{fin}}^{(j'_1, j'_2)},
\]

and it is given by

\[
\varrho_{\text{fin}}^{(j'_1, j'_2)} = \varrho_{\text{fin}}^{(j'_1)} \varrho_{\text{fin}}^{(j'_2)}.
\]

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

\[
\langle S^j_{\mu_1 \ldots \mu_l} \rangle = \langle S^j_l \rangle h_{\mu_1} \ldots h_{\mu_l},
\]

with

\[
\langle S^j_l \rangle = (2l + 1) \frac{1}{(2l + 1)!!} \sum_m N_m (j, m, l | j, m).
\]

For \( l = 0, 1, 2 \) one obtains

\[
\langle S^j_0 \rangle = \sum N_m = 1 ,
\]

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

\[
\langle S^j_2 \rangle = \sqrt{\frac{15}{2}} \left[ j(j+1) \right]^{-1/2} \sum N_m (m^2 - \frac{3}{4} j(j+1)).
\]

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

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
\[
\rho_{\text{fin}}(j_1' j_2') = \rho_{\text{fin}}^j \otimes \rho_{\text{fin}}^{j_2'}.
\] (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 \( A > A' \)) for the molecules which are in the rotational states \( j_1 \) and \( j_2 \) after the collision is given by
\[
\rho_{\text{fin}}(j_1' j_2') = a^{j_1' j_1'} a^{j_2' j_2'} \rho_{\text{fin}}^j (a' j_1' ; h h),
\] (4.14)

In Eq. (4.14), the dependence of \( \rho_{\text{fin}} \), \( a \), and \( a' \) on \( k, k', e, e' \) 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
\[
\sigma(j_1' j_2' \mid k, e, e') = k' \text{tr}_1 \text{tr}_2 \rho_{\text{fin}}(j_1' j_2').
\] (4.15)

Using Eqs. (4.13), (4.14), (4.15) and (4.6), (4.7), one gets
\[
\sigma_{\text{unpol}}(j_1' j_2', j_1' j_2') = |a_{\text{sph}}|^2 + O(\varepsilon^2),
\] (4.18a)

\[
\sigma_{\text{unpol}}(j_1' + 2 j_2', j_1' j_2') = \varepsilon^2 \frac{k}{k' + 2} \frac{3}{20} \frac{j_1' + 2}{j_1' + 1} \frac{j_1' + 1}{j_1' + 3} \text{Re}(a_{\text{sph}} A_{\mu'}^{(2)}) + O(\varepsilon^2),
\] (4.18b)

\[
\sigma_{\text{unpol}} \tilde{P}^{(j_1' j_2')}(j_1' j_2' \mid j_1' + 2 j_2') = -\varepsilon \sqrt{\frac{2}{5}} \frac{k'}{k' + 2} \frac{j_1' + 1}{3} \text{Re}(a_{\text{sph}} A_{\mu'}^{(0)}) + O(\varepsilon^2),
\] (4.18c)

\[
\sigma_{\text{unpol}} \tilde{P}^{(j_1' j_2')}(j_1' + 2 j_2' \mid j_1' j_2') = -\varepsilon^2 \frac{k}{k' + 2} \frac{3}{10} \frac{j_1' + 2}{j_1' + 1} \frac{j_1' + 1}{j_1' + 3} \frac{2 j_1' - 1}{j_1' + 1} A_{\mu'}^{(-2)} A_{\mu'}^{(-2)}
\] (4.18d)

where \( k' = \left( \frac{h^2}{2m_1} + E(j_1' + 2) - E(j_1') \right)^{1/2} \).

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 (4.20) vanish again unless the
\[
\tilde{\sigma} = \sigma_{\text{unpol}} \left( 1 + \tilde{P}^{(j_1')}_{\mu} S^{(j_1') \mu} + \cdots + \tilde{P}^{(j_1' j_2')}_{\mu_1 \ldots \mu_l} S^{\mu_1 \ldots \mu_l} \right),
\] (4.16)

where \( \sigma_{\text{unpol}} \) is the differential cross section for initially unpolarized beams, given by Eq. (1.13). The quantities
\[
\tilde{P}^{(j_1' j_2')}_{\mu_1 \ldots \mu_l} = \frac{\text{tr}_1 \text{tr}_2 \left( a^{j_1' j_1'} S^{j_1' \mu_1 \ldots \mu_l} / \text{tr}_1 \text{tr}_2 \rho_{\text{fin}}(j_1' j_2') \right)}{\text{tr}_1 \text{tr}_2 \left( a^{j_1' j_1'} S^{j_1' \mu_1 \ldots \mu_l} / \text{tr}_1 \text{tr}_2 \rho_{\text{fin}}(j_1' j_2') \right)},
\] (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. 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 \( \sigma_{\text{unpol}} \) and \( \tilde{\sigma}_{\text{unpol}} \) \( \tilde{P}^{(j_1')}_{\mu} \) 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)]
\[
\sigma_{\text{unpol}}(j_1' j_2', j_1' + 2 j_2') = |a_{\text{sph}}|^2 + O(\varepsilon^2),
\] (4.18a)

\[
\sigma_{\text{unpol}}(j_1' + 2 j_2', j_1' j_2') = \varepsilon^2 \frac{k}{k' + 2} \frac{3}{20} \frac{(j_1' + 2)(j_1' + 1)}{(2 j_1' + 3)(2 j_1' + 1)} A_{\mu'}^{(2)} A_{\mu'}^{(2)},
\] (4.18b)

\[
\sigma_{\text{unpol}} \tilde{P}^{(j_1' j_2')}(j_1' j_2' \mid j_1' + 2 j_2') = -\varepsilon \sqrt{\frac{2}{5}} \frac{k'}{k' + 2} \frac{j_1' + 1}{3} \text{Re}(a_{\text{sph}} A_{\mu'}^{(0)}) + O(\varepsilon^2),
\] (4.18c)

\[
\sigma_{\text{unpol}} \tilde{P}^{(j_1' j_2')}(j_1' + 2 j_2' \mid j_1' j_2') = -\varepsilon^2 \frac{k}{k' + 2} \frac{3}{10} \frac{(j_1' + 2)(j_1' + 1)}{(2 j_1' + 3)(2 j_1' + 1)} A_{\mu'}^{(-2)} A_{\mu'}^{(-2)}
\] (4.18d)
In the case of $H_2 - H_2$ (and of other gases for which the linear approximation of small nonsphericity is applicable) the observables
\[ \text{tr}_1 \text{tr}_2 \{ A \hat{s}_{\mu \nu} - \hat{s}_{\mu \nu} (a^\dagger) \hat{s}_{\mu \nu} \hat{S}_{\nu} \} \]
\[ = (2 j'_1 + 1) (2 j'_2 + 1) \sum_k \delta_{\text{unpol}} (j_1 j_2, j'_1 j'_2) \, P_{\mu \nu}^{j'_1 j'_2} \]
which are of importance for the Senftleben-Beenakker effect (§ 5) are of order $\varepsilon$ for energetically elastic encounters and of order $\varepsilon^2$ for collisional $j'_1 \to j'_2 \pm 2$ 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:
\[ (-1)^{j'_1 j'_2 - j_1 j_2} \hat{P}_{\mu \nu} \left( j_1 j_2, j'_1 j'_2 | \mathbf{k}, \mathbf{k}' \right) = \hat{P}_{\mu \nu} \left( j'_1 j'_2, j_1 j_2 | -\mathbf{k}', -\mathbf{k} \right). \]

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. 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 molecule.

§ 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 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 $\varepsilon^0$ which is given by $| a_{\text{ph}} |^2$ and contributions in order $\varepsilon^2$. 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 $\varepsilon^2$.

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 $\omega_{\text{tr}, \text{rot}}$ are of order $\varepsilon^2$. In particular,
\[ \omega_{\text{tr}, \text{rot}} \alpha \sum_{j_1 j_2'} (2 j_1 + 1) (2 j'_2 + 1) \cdot \left\{ \int \delta_{\text{unpol}} (j_1 j_2', j_1 j_2 | \gamma \sqrt{V, \theta} \sin \theta d\theta \right\} \, dy, \]
is very small compared with the relaxation coefficients which determine the isotropic values of the heat conductivity and viscosity. In (5.1), $\gamma = h/\sqrt{m k_B T}$ is a dimensionless relative velocity, $E(j) = E(j)/k_B T$ is the dimensionless internal energy, and
\[ \Delta E = E(j_1) + E(j_2) - E(j'_1) - E(j'_2) \]
is the dimensionless internal energy transferred in a collision. Note, that the rotational relaxation coefficient $\omega_{\text{rot}, \text{rot}}$ is proportional to $\omega_{\text{tr}, \text{rot}}$. The bulk viscosity $\eta_V$ is related to $\omega_{\text{tr}, \text{rot}}$ by
\[ \eta_V \alpha \frac{\rho}{\omega_{\text{tr}, \text{rot}}} \alpha \varepsilon^{-2}. \]
Thus $\eta_V$ will be rather large at room temperature compared with the shear viscosity which is proportional to $\varepsilon^0$.

The relaxation coefficient which couples the translational and internal energy flux is proportional to $\omega_{\text{tr}, \text{rot}}$ 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. Then also a simple Eucken relation holds.

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 tensors and $\varphi$ is an azimuthal angle which runs in a plane perpendicular to $\mathbf{e}'$.

30 If suitable (from an experimental point of view) coordinate systems are introduced (cf. Refs. 25), each of the scalar products occurring 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

velocity- and internal energy-dependent) expansion tensors with “quantum-mechanical” ones (which contain $S_{ij}$, etc., ... MIKHAILOVA (cf. Ref. 6). Notice, that the parameter $s$ defined in the present paper is $4/3$ times the $£$ used in Ref.

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

$$\frac{(\Delta \eta)_{\text{max}}}{\eta_0} = \frac{(\omega_n \tau)^2}{\eta_0 \omega_T},$$

where $\eta_0$ is the isotropic value of the viscosity, while $\omega_n$ and $\omega_T$ 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 $\omega_n \tau$ is the coupling coefficient between these tensors.

The coupling bracket

$$\omega_n \tau \propto \sum_{i,j} \exp \left( - \gamma^2 - \mathcal{E}(j_1) - \mathcal{E}(j_2) \right) \gamma^2 \gamma' \cdot \frac{\gamma^2}{\eta_0} \omega_T \cdot \left( e_{i_1} - e_{i_2} \right) \cdot \left( e_{j_1} - e_{j_2} \right)$$

is determined by the second rank tensor polarization of the molecules “1” and is of order $\epsilon^2$ due to the inelastic collisions [cf. (4.18b), (4.21)]. The elastic collisions contribute at least in order $\epsilon^2$, up to the order $\epsilon^3$, $\omega_T \propto \sum_{i,j} \exp \left( - \gamma^2 - \mathcal{E}(j_1) - \mathcal{E}(j_2) \right) \gamma^2 \gamma' \cdot \frac{\gamma^2}{\eta_0} \omega_T \cdot \left( e_{i_1} - e_{i_2} \right) \cdot \left( e_{j_1} - e_{j_2} \right)$ is a symmetric tensor in $\mathbf{e}$ and $\mathbf{e}'$ in the elastic case and $(e_{i_1} - e_{i_2} \cdot e_{j_1} - e_{j_2})$ is an antisymmetric tensor. The relaxation coefficient of the tensor polarization

$$\omega_T \propto \sum_{i,j} \exp \left( - \gamma^2 - \mathcal{E}(j_1) - \mathcal{E}(j_2) \right) \gamma^2 \gamma' \cdot \frac{\gamma^2}{\eta_0} \omega_T \cdot \left( e_{i_1} - e_{i_2} \right) \cdot \left( e_{j_1} - e_{j_2} \right)$$

is also of order $\epsilon^2$ because the generalized commutator is of order $\epsilon$. Thus the effect $\Delta \eta/\eta_0$ is of order $\epsilon^2$ and mainly determined by the inelastic collisions between the nonspherical molecules. The term in curled brackets, occurring 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. Here, one has (cf. MCCOURT and SNIDER)

$$\frac{(\Delta \lambda)_{\text{max}}}{\lambda_0} \propto \frac{(\omega_{\text{int}} K)^2}{\omega_{\text{int}} \omega_K},$$

where $\omega_{\text{int}}$ is the relaxation coefficient of the internal energy flux and $\omega_K$ is the relaxation coefficient of the “Kagan vector” $\Phi_{\mu} \propto e_{\nu} S_{\mu \nu}$. The bracket $\omega_{\text{int}} K$ couples these two vectors and $\omega_{\text{int}} K \propto \sum_{i,j} \exp \left( - \gamma^2 - \mathcal{E}(j_1) - \mathcal{E}(j_2) \right) \gamma^2 \gamma' \cdot \frac{\gamma^2}{\eta_0} \omega_T \cdot \left( e_{i_1} - e_{i_2} \right) \cdot \left( e_{j_1} - e_{j_2} \right) \cdot \left( e_{i_1} - e_{i_2} \right) \cdot \left( e_{j_1} - e_{j_2} \right)$

is an antisymmetric tensor.

Note, that the term linear in $\epsilon$ in (5.7) vanishes for $j_1 = j_2$ (o-H$_2$ in the rotational ground state). This term linear in $\epsilon$ in (5.7) is due to the elastic collisions while the contributions of $O(\epsilon^2)$ mainly stem from inelastic collisions. For p-H$_2$ at room temperature and below, the $2 + 0 \to 2 + 0$ collisions will be the most important ones. Since both relaxation coefficients $\omega_{\text{int}}$ and $\omega_K$ are of order $\epsilon^0$, the change of thermal conductivity in an applied magnetic field $\Delta \lambda/\lambda_0$ will be proportional to $\epsilon^2$ as it is true also for the change of the viscosity. This statement allows a comparison to be made of the orders of magnitude 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 $1$, $0.07$ and for HD—HD $\epsilon$ is about 0.3, the ratio $\frac{\phi_H}{\phi_H}$ is about 20. On the other hand, among the inelastic collisions in p-H$_2$ the $0 + 0 \to 2 + 0$ and $2 + 2 \to 2 + 0$ transitions will be of importance below room tempera-

$\epsilon^0$ 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.

$\epsilon^2$ 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).

Notice, that the parameter $\epsilon$ defined in the present paper is 4/3 times the $\epsilon$ used in Ref. 1.
ture, while in HD the transitions $0 + 0 \rightarrow 1 + 0$, $1 + 0 \rightarrow 2 + 0$, $1 + 1 \rightarrow 2 + 1$, $0 + 1 \rightarrow 1 + 1$ and $2 + 2 \rightarrow 1 + 2$ will give the dominant contributions. Thus the ratio $(\Delta \eta / \eta_0)_{\text{HD}} / (\Delta \eta / \eta_0)_{\text{p-H}_2}$ may still become larger, about 150, which may be due to the fact that n-H$_2$ consists of $3/4$ p-H$_2$ and $1/4$ p-H$_2$ but only ca. 12% of the o-H$_2$ molecules 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.

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 $P_{\mu L}(a, b, c)$, defined by Eq. (2.1), will be stated without derivation.

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

$$P_{\mu L+1 L'}(a, b, c) = \frac{(2l+1)!}{(l+1)!} \sum a_{\mu_1} \ldots a_{\mu_l} b_{\nu_1} \ldots b_{\nu_l} \ldots c_{\nu_1} \ldots c_{\nu_l} \ldots c_{\nu'} .$$

(A1)

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

$$P_{\mu L}(a \cdot c) P_{\nu L}(b \cdot c) = \sum_{L=|L-|} P_{\mu \nu L}(a, b, c).$$

(A2)

3) Coupling of two generalized Legendre functions yields:

$$P_{\mu L}(a, b, c) P_{k k' K}(a, b, c) = \sum_{p q R} \sqrt{2 L + 1} \sqrt{2 K + 1} \left( \frac{(0, l', 0 | 0, l, 0 K L 0), (k, k', 0 | K 0 0)}{p, q R 0} \right) \cdot \left( \frac{L K R}{L K R} \right) P_{p q R}(a, b, c),$$

where

$$\left( \begin{array}{c} l' k' p \hfill \\ L K R \end{array} \right)$$

is a 9 j-symbol.

4) An orthogonality relation (with respect to c) is:

$$\int P_{\mu L}(a, b, c) P_{k k' K}(a, b, c) d^2 c = \delta_{LK} (-1)^L \sqrt{2 L + 1} \left( \frac{(0, l', 0 | 0, l, 0 K L 0), (k, k', 0 | K 0 0)}{p, q R 0} \right) \cdot \left( \frac{L K R}{L K R} \right) P_{p q R}(a \cdot b).$$

(A4)

Finally, some properties of the Cartesian tensor operators $T_{\mu \nu L}^{ij}$ which have been defined in § 3 will be listed:

1) The hermitic adjoint of $T_{\mu \nu L}^{ij}$ is given by

$$T_{\mu \nu L}^{ij \dagger} = (-)^{j-i} T_{\mu \nu L}^{j-i} .$$

(A5)

2) The orthogonality relation is:

$$\text{tr} \left( T_{\mu \nu L}^{ij} \left( T_{\mu \nu L}^{ij} \right)^\dagger \right) = \delta_{ij} \delta_{L L'} \delta_{\mu \mu'} \delta_{\nu \nu'} .$$

(A6)


3) For \( I \leq 2 \) the following trace formulas for triple products of \( T \)-tensors hold:
\[
\text{TR}\{T^\mu_\nu T^\eta_\eta T^\phi_\phi\} = 3 \ W(j j 1 1; 2 j') A_{\nu\nu,\phi\phi},
\]
and
\[
\text{tr}\{T^\mu_\nu T^\eta_\eta T^\phi_\phi\} = -10 \ V^2 W(j j 2 2; 2 j') A_{\nu\nu,\phi\phi} A_{\eta\eta,\phi\phi} A_{\eta^r,\nu^r} A_{\phi^r,\phi^r},
\]
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.

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].