

Waldmann-Snider Collision Integrals and Nonspherical Molecular Interaction

II. DWBA-Scattering Amplitude and Cross Sections for Linear Molecules

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The binary scattering amplitude matrix is derived from the general interaction potential between linear molecules. The first order distorted wave Born approximation (DWBA) is used which is applicable for small nonsphericity of the interaction. The molecular cross sections determining the most important Waldmann-Snider collision integrals are calculated. In particular, the scattering cross section, the orientation cross sections for vector- and tensor polarization and the reorientation cross sections for the tensor polarization of the rotational angular momenta are treated. For a simple interaction model for HD (HT) molecules the DWBA-scattering amplitude is evaluated analytically. The relaxation cross section of the tensor polarization, σ^T , and the coupling cross section of friction pressure tensor and tensor polarization, $\sigma^{\eta,T}$, are calculated for room temperature and compared with experimental values.

Introduction

In a preceding paper¹, collision integrals of the linearized Waldmann-Snider^{2,3} collision (super-) operator have been discussed. They are of crucial importance for all transport and alignment phenomena in dilute molecular gases. The connection of these collision integrals with various types of molecular cross sections has been elucidated. These molecular cross sections are bilinear in the binary scattering amplitude which is a matrix with respect to the magnetic quantum numbers characterizing the degenerate rotational eigenstates of the molecules.

The present paper is concerned with the calculation of this scattering matrix from the general nonspherical interaction potential between linear molecules. The first order distorted wave Born approximation (DWBA)⁴ is used which is applicable if the nonspherical part of the interaction is small compared with the spherical part. The DWBA-scattering amplitude is subjected to a partial wave decomposition. This enables one to apply the Racah techniques to the evaluation of the various molecular cross sections. They are essentially determined by radial integrals involving the radial part of the nonspherical potential and the solutions of the scattering problem governed by the spherical potential.

In particular, the unpolarized scattering cross section, the orientation cross sections for vector-

and 2nd rank tensor polarization (separated into parts linear and quadratic in the nonsphericity) and the reorientation cross sections for arbitrary rank tensor polarization of the rotational angular momenta are studied. In the Waldmann-Snider collision integrals only cross sections integrated over the solid angle ("total cross sections") enter; the underlying differential cross sections are somewhat lengthy expressions and therefore listed in the Appendix.

As an application, the radial integrals are analytically evaluated for a simple interaction model of HD (HT) molecules ("rigid loaded spheres"). The pertaining scattering amplitude matrix is used to calculate the effective relaxation cross section of the tensor polarization¹, σ^T , and the effective coupling cross section of tensor polarization and friction pressure tensor, $\sigma^{\eta,T}$, for room temperature. No adjustable parameter appears. The results are compared with experimental values taken from the Senftleben-Beenakker effect of the viscosity⁵ and from the depolarized Rayleigh line width⁶. The agreement is good for σ^T and satisfactory for $\sigma^{\eta,T}$.

I. Nonspherical Interaction between Linear Molecules and Scattering Amplitude for Small Nonsphericity

1. Nonspherical Potential

Consider two interacting linear molecules. The vector connecting their centers of mass, pointing from molecule 2 to molecule 1 will be denoted by $\mathbf{r} = r \hat{\mathbf{r}}$ ($\hat{\mathbf{r}}$ is the corresponding unit vector). The

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unit vectors in the directions of the respective molecular axes are denoted by \mathbf{u}_1 and \mathbf{u}_2 . The intermolecular potential, as a scalar, depends on the scalars r , $\mathbf{u}_1 \cdot \hat{\mathbf{r}}$, $\mathbf{u}_2 \cdot \hat{\mathbf{r}}$, $\mathbf{u}_1 \cdot \mathbf{u}_2$. With respect to its

angular dependence it can be expanded into a complete set of functions of $\mathbf{u}_1 \cdot \hat{\mathbf{r}}$, $\mathbf{u}_2 \cdot \hat{\mathbf{r}}$, $\mathbf{u}_1 \cdot \mathbf{u}_2$. The expansion coefficients are functions of the distance r . Such a complete set is given by the functions⁷

$$P_{l'l'L}(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}) = (4\pi)^{3/2} [(2l+1)(2l'+1)(2L+1)]^{-1/2} (l0, l'0 | L0) \cdot \sum_M \left(\sum_{m, m'} (lm, l'm' | LM) Y_{lm}(\mathbf{u}_1) * Y_{l'm'}(\mathbf{u}_2) * \right) Y_{LM}(\hat{\mathbf{r}}), \quad (1.1)$$

where the Y_{lm} are spherical harmonics and $(lm, l'm' | LM)$ is a Clebsch-Gordan coefficient. Because of the Clebsch-Gordan coefficient $(l0, l'0 | L0)$ the function $P_{l'l'L}$ vanishes unless $l+l'+L$ is even and $|l-l'| \leq L \leq l+l'$. The functions (1.1) reduce in some special cases to ordinary Legendre functions and may thus be called "Generalized Legendre Functions". These special cases are

$$P_{l0L}(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}) = P_L(\mathbf{u}_1 \cdot \hat{\mathbf{r}}) \delta_{lL}, \quad (1.2a)$$

$$P_{0lL}(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}) = P_L(\mathbf{u}_2 \cdot \hat{\mathbf{r}}) \delta_{lL}, \quad (1.2b)$$

$$P_{l'l'0}(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}) = (2l+1)^{-1} P_l(\mathbf{u}_1 \cdot \mathbf{u}_2) \delta_{l'l'}. \quad (1.2c)$$

In particular, one has $P_{000}(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}) \equiv 1$.

The nonspherical potential $V(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r})$ is expanded as follows:

$$V(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = \sum_{L=0}^{\infty} \sum_{l, l'=0}^{\infty} V^{l'l'L}(r) P_{l'l'L}(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}) = V_0(r) + V_{\text{nsp}}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}), \quad (1.3)$$

where $V_0(r) \equiv V_{000}(r)$ is the spherical part and V_{nsp} is the nonspherical part of the potential which is obtained if in (1.3) only pairs $(l, l') \neq (0, 0)$ are considered. As examples, two terms of the series (1.3) represent the dipole-dipole and the quadrupole-quadrupole interactions, viz.

$$V_{d,d}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = -3 d_1 d_2 r^{-3} P_{112}(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}), \quad (1.4)$$

where d_1, d_2 are the molecular dipole moments, and

$$V_{Q,Q}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = \frac{35}{12} Q_1 Q_2 r^{-5} P_{224}(\mathbf{u}_1, \mathbf{u}_2, \hat{\mathbf{r}}), \quad (1.5)$$

where Q_1, Q_2 are the molecular quadrupole moments. Expressions for the dispersion potential⁸ (interaction between induced multipoles) and the induction potential⁸ (interaction between perma-

nent and induced multipoles) in terms of the $P_{l'l'L}$ have been given in Reference⁷. The radial coefficients $V^{l'l'L}(r)$ are thus known to some extent for the long range part of the interaction, but very little information is available on the short range part of the potential. Here often models (Morse potential, Lennard-Jones potential) are used. The nonspherical potential (at least its short range part) is then often approximated by the first terms of the series (1.3),

$$V(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = V_0(r) + V^L(r) [P_L(\mathbf{u}_1 \cdot \hat{\mathbf{r}}) + (-1)^L P_L(\mathbf{u}_2 \cdot \hat{\mathbf{r}})], \quad (1.6)$$

with suitable functions $V_0(r)$ and $V^L(r)$. Since for homonuclear molecules the potential must be symmetric with respect to an interchange $\mathbf{u}_1 \longleftrightarrow -\mathbf{u}_1$, $\mathbf{u}_2 \longleftrightarrow -\mathbf{u}_2$, one has $L=2$ while for heteronuclear molecules $L=1$ should be taken.

The form of the potential (1.6) can be well understood in the case of molecules with small excentricity of their center of mass, e.g. HD⁹: It is assumed that the potential between H₂ molecules and HD molecules is the same considered as a function of the vector connecting the geometric centers of the molecules (because of the same electron cloud). If the H₂-H₂ potential is taken as spherical and is, for HD, transformed into a function of the vector connecting the centers of mass one finds the potential

$$V(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = V_0(r) + (\partial V_0 / \partial r) d [P_1(\mathbf{u}_1 \cdot \hat{\mathbf{r}}) - P_1(\mathbf{u}_2 \cdot \hat{\mathbf{r}})] \quad (1.7)$$

as a Taylor expansion up to terms linear in the excentricity d . The spherical H₂-H₂ potential has been denoted by V_0 . The excentricity d is determined by the equilibrium distance b of the atoms in the molecule and by the atomic masses m_1 and m_2 :

$$d = b(m_2 - m_1) / 2(m_2 + m_1). \quad (1.8)$$

A potential of the form (1.7) with suitable $V_0(r)$ will be used in Sect. III in explicit calculations for HD and HT.

2. Scattering Amplitude in the Approximation of small Nonsphericity

To develop a scattering theory for linear molecules we first introduce a nonsphericity parameter ε by

$$V_{\text{nsph}} = \varepsilon \mathcal{V} \quad (1.9)$$

where \mathcal{V} is assumed to be of the same order of magnitude as the spherical potential V_0 . If the nonspherical part of the potential is small compared with the spherical part on the average (e.g. if $|\int_0^\infty V_{\text{nsph}} dr| \ll |\int_0^\infty V_0 dr|$ provided that the integrals exist) one has $\varepsilon \ll 1$. In the following we restrict ourselves to this case of small nonsphericity.

The binary scattering operator T is connected with the interaction potential V of Eq. (1.3) by the operator equation⁴

$$T = V + V(E - H + i\eta)^{-1}V, \quad \eta \rightarrow +0 \quad (1.10)$$

("formal solution" of the Lippmann-Schwinger equation). The total energy of the molecules is E and $H = K + H_{\text{int}} + V_0 + V_{\text{nsph}}$ is the total Hamiltonian; $(E - H + i\eta)^{-1}$ is the pertaining Green's operator for outgoing spherical waves at infinity. The operator of the kinetic energy of the relative motion is K and $H_{\text{int}} = \hbar^2 (J_1^2 + J_2^2)/2\Theta$ is the internal rotational Hamiltonian of the linear molecules with rotational angular momenta $\mathbf{J}_1, \mathbf{J}_2$ and moment of inertia Θ .

As $\varepsilon \ll 1$ is assumed, an expansion of T in powers of ε can be truncated after the term linear in ε :

$$T = T_0 + \varepsilon T_1 + O(\varepsilon^2). \quad (1.11)$$

Insertion of (1.11) and (1.9) into Eq. (1.10) and comparison of terms with equal power in ε yields

$$T_0 = V_0 + V_0(E - H_0 + i\eta)^{-1}V_0, \quad (1.12)$$

$$\varepsilon T_1 = [1 + V_0(E - H_0 + i\eta)^{-1}] V_{\text{nsph}} [1 + (E - H_0 + i\eta)^{-1}V_0]. \quad (1.13)$$

Here $H_0 = K + H_{\text{int}} + V_0$ is the Hamiltonian corresponding to a spherical interaction and $(E - H_0 + i\eta)^{-1}$ is the pertaining Green's operator. Equation (1.12) represents the formal solution of the Lippmann-Schwinger equation for the scattering problem governed by the spherical potential V_0 . In the approximation of small nonsphericity, expressed by Eqs. (1.11) – (1.13) the scattering operator T_0 has to be calculated exactly and the non-

sphericity is treated in first order perturbation theory.

The scattering amplitude $a(\mathbf{k}, \mathbf{k}')$ is connected with the T -operator by

$$a(\mathbf{k}, \mathbf{k}') = - (m_{12}/2\pi\hbar^2) \langle \mathbf{k} | T | \mathbf{k}' \rangle, \quad (1.14)$$

where $\langle \mathbf{r} | \mathbf{k} \rangle = \exp\{i\mathbf{k} \cdot \mathbf{r}\}$ is a plane wave and $m_{12} = m/2$ is the reduced mass. By use of the two particle projection operator $P^{j_1 j_2}$ acting in rotational angular momentum space

$$P^{j_1 j_2} = \sum_{m_1, m_2} |j_1 m_1, j_2 m_2\rangle \langle j_1 m_1, j_2 m_2|$$

($|j_1 m_1, j_2 m_2\rangle$ being eigenstates of H_{int}) the single channel scattering amplitude

$$a^{j_1 j_2, j_1' j_2'} = P^{j_1 j_2} a P^{j_1' j_2'} \quad (1.15)$$

is introduced. It describes a transition $j_1' + j_2' \rightarrow j_1 + j_2$ in rotational quantum numbers, is still a matrix with respect to magnetic quantum numbers and is the quantity which essentially determines the Waldmann-Snider collision term¹. After Eqs. (1.11), (1.14), (1.15) it can be decomposed into two parts:

$$a^{j_1 j_2, j_1' j_2'} = a_0 P^{j_1 j_2} \delta^{j_1 j_1'} \delta^{j_2 j_2'} + a_1^{j_1 j_2, j_1' j_2'}. \quad (1.16)$$

In Eq. (1.16), the first term

$$a_0(\mathbf{k}, \mathbf{k}') = - (m_{12}/2\pi\hbar^2) \langle \mathbf{k} | T_0 | \mathbf{k}' \rangle \quad (1.17)$$

is the scattering amplitude due to a purely spherical potential. The δ -symbols and the projection operator occurring in (1.16) express that the spherical part of the interaction cannot induce transitions between different rotational eigenstates. The second term

$$a_1^{j_1 j_2, j_1' j_2'}(\mathbf{k}, \mathbf{k}') = - (m_{12}/2\pi\hbar^2) \cdot \varepsilon \langle \mathbf{k} | T_1^{j_1 j_2, j_1' j_2'} | \mathbf{k}' \rangle, \quad (1.18)$$

with $T_1^{j_1 j_2, j_1' j_2'} = P^{j_1 j_2} T_1 P^{j_1' j_2'}$, is the part of the scattering amplitude connected with the nonsphericity of the interaction.

Since the operator $(E - H_0 + i\eta)^{-1}$ is diagonal in the rotational eigenstates one has

$$(E - H_0 + i\eta)^{-1} |j_1 m_1, j_2 m_2\rangle = (\hbar^2 k^2/2m_{12} - K - V_0 + i\eta)^{-1} |j_1 m_1, j_2 m_2\rangle. \quad (1.19)$$

In (1.19), $\hbar^2 k^2/2m_{12} \equiv E - E(j_1) - E(j_2)$ denotes the kinetic energy of the relative motion after the collision and

$$E(j) = \hbar^2 j(j+1)/2\Theta \quad (1.20)$$

the internal energy of a molecule in the rotational state j . It is now convenient to introduce states

$$|\chi_{\mathbf{k}}^{(\pm)}\rangle \equiv [1 + (\hbar^2 k^2 / 2 m_{12} - K - V_0 \pm i \eta)^{-1} V_0] |\mathbf{k}\rangle \quad (1.21)$$

which are solutions of the scattering problem governed by the spherical potential V_0 and which obey the boundary condition of plane waves plus out (in-) going spherical waves at infinity. By use of Eqs.

(1.12), (1.13), (1.21), Eq. (1.17) can be rewritten as

$$a_0(\mathbf{k}, \mathbf{k}') = - (m_{12} / 2 \pi \hbar^2) \langle \mathbf{k} | V_0 | \chi_{\mathbf{k}'}^{(+)} \rangle \quad (1.22)$$

$$\text{with} \quad k'^2 = k^2. \quad (1.22 \text{ a})$$

In the same way and with (Eq. (1.3) the “non-spherical” scattering amplitude, Eq. (1.18) can be written as¹⁰

$$a_1^{j_1 j_2, j_1' j_2'}(\mathbf{k}, \mathbf{k}') = - (m_{12} / 2 \pi \hbar^2) \sum_L \sum_{l, l'} \langle \chi_{\mathbf{k}}^{(-)} | V^{LL}(r) P_{l l'}^{j_1 j_2, j_1' j_2'} | \chi_{\mathbf{k}'}^{(+)} \rangle \quad (1.23)$$

$$\text{with} \quad k'^2 = k^2 + (2 m_{12} / \hbar^2) [E(j_1) + E(j_2) - E(j_1') - E(j_2')]. \quad (1.23 \text{ a})$$

For further evaluation of the term $P_{l l'}^{j_1 j_2, j_1' j_2'}$ the “projected spherical harmonics” $Y_{lm}^{* j j'} = P^j Y_{lm}^* P^{j'}$ have to be considered. With Clebsch-Gordan algebra one obtains⁷

$$Y_{lm}^* (\mathbf{u})^{j j'} = \sqrt{(2j+1)/4\pi} \langle j 0, l 0 | j' 0 \rangle T_{lm}^{j j'}, \quad (1.24)$$

where $T_{lm}^{j j'}$ is a spherical tensor operator of rank l acting on rotational states. It is defined by

$$T_{lm}^{j j'} = \sum_{m', m''} (-1)^{j-m''} \langle j' m', j-m'' | l m \rangle | j m'' \rangle \langle j' m' |. \quad (1.25)$$

Properties of these tensor operators are listed in the Appendix A. Observing Eqs. (1.1), (1.25), we can again rewrite Eq. (1.23) as

$$a_1^{j_1 j_2, j_1' j_2'}(\mathbf{k}, \mathbf{k}') = - \frac{m_{12}}{\sqrt{\pi} \hbar^2} \sum_L \sum_{l, l'} \left(\frac{(2j_1+1)(2j_2+1)}{(2l+1)(2l'+1)(2L+1)} \right)^{1/2} \cdot (j_1 0, l 0 | j_1' 0) (j_2 0, l' 0 | j_2' 0) (l 0, l' 0 | L 0) \sum_M \sum_{m, m'} (l m, l' m' | L M) T_{lm}^{j_1 j_2} T_{l'm'}^{j_1' j_2'} \langle \chi_{\mathbf{k}}^{(-)} | V^{LL}(r) Y_{LM}(\hat{\mathbf{r}}) | \chi_{\mathbf{k}'}^{(+)} \rangle. \quad (1.26)$$

The first two Clebsch-Gordan coefficients in (1.26) vanish unless

$$\begin{aligned} |j_1 - j_1'| &\leq l \leq j_1 + j_1', & j_1 + j_1' + l &\text{even}, \\ |j_2 - j_2'| &\leq l' \leq j_2 + j_2', & j_2 + j_2' + l' &\text{even}. \end{aligned} \quad (1.27)$$

Equation (1.27) expresses the selection rules for the rotational transitions.

For a simplified potential Eq. (1.6) (pure P_L -terms) one has only two contributions, viz. for $l=L, l'=0$ and $l'=L, l=0$. In this case the scattering amplitude (1.26) reduces to

$$a_1^{j_1 j_2, j_1' j_2'}(\mathbf{k}, \mathbf{k}') = - [m_{12} / \pi \hbar^2 (2L+1)] \sum_M [\sqrt{2j_1+1} (j_1 0, L 0 | j_1' 0) T_{LM}^{j_1 j_2} P_{L0} \delta_{j_2 j_2'} + (-1)^L \sqrt{2j_2+1} (j_2 0, L 0 | j_2' 0) T_{LM}^{j_2 j_2'} P_{L0} \delta_{j_1 j_1'}] \langle \chi_{\mathbf{k}}^{(-)} | V^L(r) Y_{LM}(\hat{\mathbf{r}}) | \chi_{\mathbf{k}'}^{(+)} \rangle. \quad (1.28)$$

Because of the δ -symbols, only one of both molecules can change its rotational state in a collision.

3. Partial Wave Decomposition of the DWBA Scattering Amplitude

For the calculation of cross sections it is useful to decompose the scattering amplitude into partial amplitudes. This allows the separation of the scattering geometry from the dynamics. For the “spherical part” a_0 of Eq. (1.17) this is a well known procedure⁴ ending in

$$a_0(k, \mathbf{e} \cdot \mathbf{e}') = \frac{4\pi}{k} \sum_{l=0}^{\infty} e^{i\delta_l(k)} \sin \delta_l(k) \sum_m Y_{lm}^*(\mathbf{e}) Y_{lm}(\mathbf{e}'). \quad (1.29)$$

Here, \mathbf{e} and \mathbf{e}' are the directions of the wave vectors \mathbf{k} and \mathbf{k}' , respectively, and $\delta_l(k)$ are the phase shifts produced by the spherical potential. For a corresponding treatment of the “nonspherical” scattering amplitude a_1 of Eq. (1.26), the distorted waves have to be decomposed into partial waves:

$$\chi_{\mathbf{k}'}^{(+)}(\mathbf{r}) = 4\pi \sum_{l=0}^{\infty} i^l \chi_l^{(+)}(k', r) \sum_m Y_{lm}^*(\mathbf{e}') Y_{lm}(\hat{\mathbf{r}}). \quad (1.30)$$

The partial waves $\chi_l^{(+)}(k', r)$ are solutions of the radial Schrödinger equation

$$\{ \Delta_r + k'^2 - l(l+1)/r^2 - 2m_{12} V_0(r)/\hbar^2 \} \chi_l^{(+)}(k', r) = 0. \quad (1.31)$$

They obey the boundary condition at infinity

$$\chi_l^{(+)}(k', r) \underset{r \rightarrow \infty}{\sim} j_l(k' r) + (i^{-l}/k' r) e^{i\delta_l} \sin \delta_l e^{ik' r}, \quad (1.32)$$

where $j_l(k' r)$ is a spherical Bessel function. The partial wave expansion of the plane wave $\exp\{i\mathbf{k}' \cdot \mathbf{r}\}$ is obtained from (1.30) if one replaces $\chi_l^{(+)}(k', r)$ by $j_l(k' r)$.

Now we insert the expansion Eq. (1.30) for $\chi_{\mathbf{k}'}^{(+)}(\mathbf{r})$ (with λ' as summation index) and the corresponding one for $\chi_{\mathbf{k}}^{(-)}(\mathbf{r})$ (with λ as summation index) into Equation (1.26). If we observe the relation⁴

$$\chi_{\mathbf{k}}^{(-)}(\mathbf{r})^* = \chi_{-\mathbf{k}}^{(+)}(\mathbf{r}),$$

we obtain the following expression for the relevant matrix element occurring in Eq. (1.26)

$$\begin{aligned} \langle \chi_{\mathbf{k}}^{(-)} | V^{ll'L}(r) Y_{LM}(\hat{\mathbf{r}}) | \chi_{\mathbf{k}'}^{(+)} \rangle &= (4\pi)^{3/2} (2L+1)^{-1/2} \sum_{\lambda, \lambda'=0}^{\infty} \{ V_{\lambda\lambda'}^{ll'L}(k, k') \\ &\cdot i^{\lambda'-\lambda} \sqrt{(2\lambda+1)(2\lambda'+1)} (\lambda 0, \lambda' 0 | L 0) \sum_{\mu, \mu'} (\lambda \mu, \lambda' \mu' | LM) Y_{\lambda\mu}(\mathbf{e}) Y_{\lambda'\mu'}(\mathbf{e}') \}. \end{aligned} \quad (1.33)$$

In Eq. (1.33), the spherical harmonics and the Clebsch-Gordan coefficients represent the scattering geometry while the dynamics are contained in the radial integrals

$$V_{\lambda\lambda'}^{ll'L}(k, k') = V_{\lambda\lambda'}^{ll'L}(k', k) = \int_0^{\infty} \chi_{\lambda}^{(+)}(k, r) V^{ll'L}(r) \chi_{\lambda'}^{(+)}(k', r) r^2 dr, \quad (1.34)$$

which involve the radial parts of the nonspherical interaction and the partial distorted waves. In the case of energetically elastic scattering ($k^2 = k'^2$) one has

$$V_{\lambda\lambda'}^{ll'L}(k) = V_{\lambda'\lambda}^{ll'L}(k).$$

Notice that $|\lambda - \lambda'| \leq L \leq \lambda + \lambda'$ and that $\lambda + \lambda' + L$ has to be even. In Sect. III the integral (1.34) will be evaluated analytically for a simple potential model (“rigid loaded spheres”) for HD(HT) molecules.

II. Molecular Cross Sections

In this section the molecular cross sections determining the Waldmann-Snider collision integrals (cf. I) are calculated from the DWBA scattering amplitude Equation (1.16). By use of its partial wave decomposition, Eq. (1.33), and some Racah algebra the cross sections can be given as Legendre-polynomial series $\sum a_R P_R(\cos\vartheta)$, where $\vartheta = \arccos \mathbf{e} \cdot \mathbf{e}'$ is the angle of deflection. The expressions for these differential cross sections are a little bit lengthy. Therefore it seems to be reasonable to present in this section only total cross sections (differential cross sections integrated over the solid angle) explicitly. Indeed, only these are needed for the collision integrals. The underlying differential cross sections are listed in the Appendix B.

1. Scattering Cross Section

First, the differential scattering cross section

$$\sigma(j_1 j_2, j_1' j_2') = (k'/k) (2j_1+1)^{-1} (2j_2+1)^{-1} \text{tr}_1 \text{tr}_2 [a^{j_1 j_2, j_1' j_2'} a^{\dagger j_1' j_2', j_1 j_2}] \quad (2.1) \text{ and (I 2.20)}$$

is considered. It equals the “unpolarized” differential scattering cross section for the inverse collision process $j_1 + j_2 \rightarrow j_1' + j_2'$ averaged over initial and summed over final magnetic quantum numbers. The trace

in spin space is denoted by "tr". Here and in the following we refrain from explicitly writing down the arguments k, ϑ . From Eq. (1.16) one infers that

$$\sigma(j_1 j_2, j_1' j_2') = \sigma_0 \delta_{j_1 j_1'} \delta_{j_2 j_2'} + \sigma_1(j_1 j_2, j_1' j_2'), \quad (2.2)$$

$$\text{with } \sigma_0 = |a_0|^2, \quad (2.3 \text{ a})$$

$$\sigma_1 = \frac{k'}{k} (2j_1 + 1)^{-1} (2j_2 + 1)^{-1} \text{tr}_1 \text{tr}_2 [a_1^{j_1 j_2, j_1' j_2'} a_1^{\dagger j_1' j_2', j_1 j_2}]. \quad (2.3 \text{ b})$$

Here, a_0 is given by Eq. (1.29) and a_1 by Eq. (1.26). Note that a contribution to σ bilinear in a_0 and a_1 does not occur. This follows from

$$\text{tr}_1 \text{tr}_2 [a_1^{j_1 j_2, j_1' j_2'}] = 0,$$

which is due to Eq. (1.26) and the trace property (A 2).

After Eq. (1.29), the total scattering cross section in "spherical approximation", $2\pi \int \sigma_0 \sin \vartheta d\vartheta$, is fully determined by the phase shifts δ_l . For the calculation of σ_1 which is of second order in the non-sphericity some Racah algebra is necessary (cf. Appendix B). The collision integrals determining the scalar transport phenomena contain in general total cross sections of the form

$$2\pi \int_0^\pi \sigma(j_1 j_2, j_1' j_2') P_K(\cos \vartheta) \sin \vartheta d\vartheta.$$

The part involving the cross section σ_0 is well known^{11, 12} for $K=0, 1, 2$. From (B 1) one obtains

$$2\pi \int_0^\pi \sigma_1 P_K(\cos \vartheta) \sin \vartheta d\vartheta = \frac{4\pi m^2 k'}{\hbar^4 (2K+1)k} \sum_L \sum_{l, l'} (j_1 0, l 0 | j_1' 0)^2 (j_2 0, l' 0 | j_2' 0)^2 \sum_{\lambda \lambda' \lambda_1 \lambda_1'} A_{\lambda \lambda' \lambda_1 \lambda_1'}^{l l' L K} \text{Re} [V_{\lambda \lambda'}^{l l' L} V_{\lambda_1 \lambda_1'}^{l l' L*}]. \quad (2.4)$$

The $A_{\lambda \lambda' \lambda_1 \lambda_1'}^{l l' L K}$ are geometry coefficients given by

$$A_{\lambda \lambda' \lambda_1 \lambda_1'}^{l l' L K} = [(2l+1)(2l'+1)(2L+1)]^{-1} (l 0, l' 0 | L 0)^2 (\lambda 0, \lambda' 0 | L 0) (\lambda_1 0, \lambda_1' 0 | L 0) (\lambda 0, \lambda_1 0 | K 0) (\lambda_1' 0, \lambda_1' 0 | K 0) (2\lambda+1)(2\lambda'+1)(2\lambda_1+1)(2\lambda_1'+1) (-1)^{(\lambda+\lambda'+\lambda_1+\lambda_1')/2} W(\lambda \lambda_1 \lambda' \lambda_1'; K L), \quad (2.5)$$

where $W(\dots)$ is a Racah coefficient¹³ and $\lambda+\lambda'+\lambda_1+\lambda_1'$ is even.

To achieve a shorter notation the arguments $j_1 \dots j_2'$ are omitted in the l.h.s. of equations expressing total cross sections.

The important special case $K=0$ of Eq. (2.4) yields the total cross section the inelastic part of which determines the temperature relaxation coefficient¹:

$$2\pi \int_0^\pi \sigma_1 \sin \vartheta d\vartheta = \frac{4\pi m^2 k'}{\hbar^4 k} \sum_L \sum_{l, l'} [(2l+1)(2l'+1)(2L+1)]^{-1} (j_1 0, l 0 | j_1' 0)^2 (j_2 0, l' 0 | j_2' 0)^2 (l 0, l' 0 | L 0)^2 \sum_{\lambda \lambda'} (2\lambda+1)(2\lambda'+1) (\lambda 0, \lambda' 0 | L 0)^2 |V_{\lambda \lambda'}^{l l' L}|^2. \quad (2.6)$$

For a pure P_L -potential as given by Eq. (1.6), Eq. (2.6) reduces to

$$2\pi \int_0^\pi \sigma_1 \sin \vartheta d\vartheta = \frac{4\pi m^2 k'}{\hbar^4 (2L+1)^2 k} [(j_1 0, L 0 | j_1' 0)^2 \delta_{j_2 j_2'} + (j_2 0, L 0 | j_2' 0)^2 \delta_{j_1 j_1'}] \cdot \sum_{\lambda \lambda'} (2\lambda+1)(2\lambda'+1) (\lambda 0, \lambda' 0 | L 0)^2 |V_{\lambda \lambda'}^{L 0 L}|^2. \quad (2.7)$$

For the case $L=1$ which is explicitly treated in Sect. III, the λ' -summation gives

$$\sum_{\lambda \lambda'} (2\lambda+1)(2\lambda'+1) (\lambda 0, \lambda' 0 | L 0)^2 |V_{\lambda \lambda'}^{L 0 L}|^2 = 3 \sum_{\lambda=0}^{\infty} (\lambda+1) (|V_{\lambda \lambda+1}^{1 0 1}|^2 + |V_{\lambda+1 \lambda}^{1 0 1}|^2). \quad (2.8)$$

Equation (2.7) together with Eq. (2.8) is analogous to the well known expressions for the total transport cross sections in terms of phase shifts occurring with the monatomic Boltzmann equation¹², and is appropriate for numerical evaluation.

2. Orientation Cross Sections for Vector- and Tensor Polarization

The orientation cross sections for vector and 2nd rank tensor polarization are of crucial importance for all direct and indirect nonequilibrium alignment phenomena¹. They determine the ensuing coupling coefficients between classical moments (heat fluxes, friction pressure tensor) and rotational angular momentum polarizations. The relevant orientation cross sections, introduced in I, are:

Orientation cross section for the vector polarization

$$\sigma_n^{(1)}(j_1 j_2, j_1' j_2') = (2j_1 + 1)^{-1} (2j_2 + 1)^{-1} \frac{k'}{k} \sqrt{3} \operatorname{tr}_1 \operatorname{tr}_2 [a^{j_1 j_2, j_1' j_2'} a^{\dagger j_1' j_2', j_1 j_2} \mathbf{J}_1 \cdot \mathbf{n}], \quad (2.9)$$

with $\mathbf{n} = \mathbf{e}' \times \mathbf{e} / \sin \vartheta$ being a unit vector normal to the scattering plane.

Orientation cross sections for the tensor polarization*

$$\sigma_{ee}^{(1)}(j_1 j_2, j_1' j_2') = (2j_1 + 1)^{-1} (2j_2 + 1)^{-1} (k'/k) \sqrt{\frac{15}{2}} \operatorname{tr}_1 \operatorname{tr}_2 [a^{j_1 j_2, j_1' j_2'} a^{\dagger j_1' j_2', j_1 j_2} \overline{J_{1\mu} J_{1\nu}} e_\mu e_\nu], \quad (2.10)$$

$$\sigma_{ee'}^{(1)}(j_1 j_2, j_1' j_2') = (2j_1 + 1)^{-1} (2j_2 + 1)^{-1} (k'/k) \sqrt{\frac{15}{2}} \operatorname{tr}_1 \operatorname{tr}_2 [a^{j_1 j_2, j_1' j_2'} a^{\dagger j_1' j_2', j_1 j_2} \overline{J_{1\mu} J_{1\nu}} e_\mu e_{\nu'}], \quad (2.11)$$

and $\sigma_{ee'}^{(1)}$. The superscript 1 refers to the polarization of particles 1 (\mathbf{J}_1 occurs under the trace!) after the collision.

For the further treatment it is convenient to write the scalar products occurring in Eqs. (2.9) – (2.11) in spherical rather than in Cartesian tensor notation in order to apply the Racah technique. The following equalities have to be observed:

$$P^j \mathbf{J} \cdot \mathbf{n} P^j \sin \vartheta = \frac{4\pi i}{3} \sqrt{\frac{2(2j+1)}{3}} g_0(j) \sum_{q q' Q} (1 q, 1 q' | 1 Q) Y_{1q}(\mathbf{e}) Y_{1q'}(\mathbf{e}') T_{1Q}^{jj}, \quad (2.12)$$

$$P^j \overline{J_\mu J_\nu} P^j e_\mu e_\nu = \frac{2}{15} \sqrt{4\pi(2j+1)} g_1(j) \sum_Q Y_{2Q}(\mathbf{e}) T_{2Q}^{jj}, \quad (2.13)$$

and

$$P^j \overline{J_\mu J_\nu} P^j e_\mu e_{\nu'} = \frac{4\pi}{3} \sqrt{\frac{2(2j+1)}{15}} g_1(j) \sum_{q q' Q} (1 q, 1 q' | 2 Q) Y_{1q}(\mathbf{e}) Y_{1q'}(\mathbf{e}') T_{2Q}^{jj}. \quad (2.14)$$

The abbreviation

$$g_l^2(j) = \prod_{l'=0}^l \left[j(j+1) - \frac{l'}{2} \left(\frac{l'}{2} + 1 \right) \right] \quad (2.15) \quad \text{and (I 2.34)}$$

has been used. Furthermore, it is appropriate to introduce the spherical K^{th} rank orientation cross section tensor

$$\sigma_{KK}^{(1)}(j_1 j_2, j_1' j_2') = (2j_1 + 1)^{-1} (2j_2 + 1)^{-1} (k'/k) \operatorname{tr}_1 \operatorname{tr}_2 [a^{j_1 j_2, j_1' j_2'} a^{\dagger j_1' j_2', j_1 j_2} T_{KK}^{j_1 j_2}]. \quad (2.16)$$

From Eqs. (2.12) – (2.14) the notation of the orientation cross sections (2.9) – (2.11) in terms of $\sigma_{1Q}^{(1)}$, $\sigma_{2Q}^{(1)}$ is then obvious and we refrain from writing down the corresponding expressions.

a) Contributions linear in the nonsphericity

For energetically elastic collisions an interference term between spherical and nonspherical parts of the scattering amplitude occurs in (2.16):

$$\sigma_{KK}^{(1)}(j_1 j_2) = (2j_1 + 1)^{-1} (2j_2 + 1)^{-1} \operatorname{tr}_1 \operatorname{tr}_2 [(a_0^* a_1^{j_1 j_2, j_1 j_2} + a_0 a_1^{\dagger j_1 j_2, j_1 j_2}) T_{KK}^{j_1 j_2}]. \quad (2.17)$$

It is responsible for orientation cross sections linear in the nonsphericity which are indicated by the left subscript 1 (order of nonsphericity). From Eqs. (1.26) and (A 2) follows that (2.17) vanishes unless $l = L = K$

* The sign “—” refers to the symmetric traceless part of a tensor.

and $l' = 0$. Using Eqs. (1.29) and (1.33) and Racah algebra we obtain

$${}_1\sigma_{KQ}^{(1)}(j_1) = -\frac{8\pi m}{\hbar^2 k} (2K+1)^{-3/2} (2j_1+1)^{-1/2} (j_1 0, K 0 | j_1 0) \sum_{\lambda \lambda' \lambda_1 \lambda_1' \lambda_2} B_{\lambda \lambda' \lambda_1 \lambda_1' K \lambda_2} \text{Re}[e^{-i\delta_{\lambda_2}} \sin \delta_{\lambda_2} V_{\lambda \lambda'}^{K0K}] \sum_{\mu_1 \mu_1'} (\lambda_1 \mu_1, \lambda_1' \mu_1' | K Q) Y_{\lambda_1 \mu_1}(\mathbf{e}) Y_{\lambda_1' \mu_1'}(\mathbf{e}'). \quad (2.18)$$

In (2.18), $B_{\lambda \lambda' \lambda_1 \lambda_1' K \lambda_2}$ is a geometry coefficient given by

$$B_{\lambda \lambda' \lambda_1 \lambda_1' K \lambda_2} = (2\lambda+1)(2\lambda'+1)(2\lambda_2+1)(-1)^{\lambda_2+(\lambda+\lambda')/2} (\lambda 0, \lambda' 0 | K 0) (\lambda 0, \lambda_2 0 | \lambda_1 0) (\lambda' 0, \lambda_2 0 | \lambda_1' 0) W(\lambda \lambda' \lambda_1 \lambda_1'; K \lambda_2). \quad (2.19)$$

Since this coefficient is symmetric with respect to an interchange $\lambda \longleftrightarrow \lambda'$, $\lambda_1 \longleftrightarrow \lambda_1'$, and since $V_{\lambda \lambda'}^{K0K} = V_{\lambda' \lambda}^{K0K}$ one can easily show from (2.18) that ${}_1\sigma_{KQ}^{(1)}$ is symmetric in \mathbf{e} and \mathbf{e}' .

For $K=1$ the coefficient $(j_1 0, 10 | j_1 0)$ vanishes. This implies that

$${}_1\sigma_n^{(1)} = 0, \quad (2.20)$$

i. e. there is no orientation cross section for the vector polarization linear in the nonsphericity. After (I. 3.38), the coupling between azimuthal polarization and rotational heat flux is at least quadratic in the nonsphericity.

For $K=2$ one has $(j_1 0, 20 | j_1 0) = -\frac{1}{2} g_0^2(j_1)/g_1(j_1)$ and ${}_1\sigma_{2Q}^{(1)}$ is nonzero if the intermolecular potential contains a $P_2(\mathbf{u}_1 \cdot \hat{\mathbf{r}})$ -term. As a consequence, nonvanishing orientation cross sections ${}_1\sigma_{ee}^{(1)}$, ${}_1\sigma_{e'e'}^{(1)}$, and ${}_1\sigma_{ee'}^{(1)}$ exist. But only two of them have to be considered since from the symmetry of ${}_1\sigma_{2Q}^{(1)}$ in \mathbf{e} and \mathbf{e}' also the following symmetry relation can be derived:

$${}_1\sigma_{e'e'}^{(1)} = {}_1\sigma_{ee}^{(1)}. \quad (2.21)$$

From Eqs. (2.18), (2.13), (2.14) and (B 3, 4) and after evaluation of the solid angle integration and the λ -summations as far as possible one obtains the total orientation cross sections needed for the Waldmann-Snider collision integrals:

$$2\pi \int_0^\pi {}_1\sigma_{ee}^{(1)} \sin \vartheta d\vartheta = \frac{6\pi m}{\hbar^2 k} V_{15}^{-2} j_1(j_1+1) \sum_{\lambda=0}^\infty \frac{(\lambda+1)(\lambda+2)}{2\lambda+3} \left\{ \frac{2(2\lambda+3)^2}{3(2\lambda+1)(2\lambda+5)} \text{Re}[e^{-i\delta_{\lambda+1}} \sin \delta_{\lambda+1} V_{\lambda+1\lambda+1}^{202}] - \text{Re}[(e^{-i\delta_\lambda} \sin \delta_\lambda + e^{-i\delta_{\lambda+2}} \sin \delta_{\lambda+2}) V_{\lambda\lambda+2}^{202}] \right\}, \quad (2.22)$$

and

$$2\pi \int_0^\pi {}_1\sigma_{e'e'}^{(1)} \sin \vartheta d\vartheta = \frac{2\pi m}{\hbar^2 k} V_{15}^{-2} j_1(j_1+1) \sum_{\lambda=0}^\infty \frac{(\lambda+1)(\lambda+2)}{2\lambda+3} \left\{ \frac{2\lambda+3}{2\lambda+1} \text{Re}[e^{-i\delta_\lambda} \sin \delta_\lambda V_{\lambda+1\lambda+1}^{202}] + \frac{2\lambda+3}{2\lambda+5} \text{Re}[e^{-i\delta_{\lambda+2}} \sin \delta_{\lambda+2} V_{\lambda+1\lambda+1}^{202}] - 6 \text{Re}[e^{-i\delta_{\lambda+1}} \sin \delta_{\lambda+1} V_{\lambda\lambda+2}^{202}] \right\}. \quad (2.23)$$

The expressions (2.22) and (2.23) have previously been used by the author¹⁴ to calculate the effective coupling cross section of the Kagan vector¹ and the rotational heat flux, ${}_e\sigma^K, q_{rot}$ (I 3.42), for $p-H_2$ at room temperature.

b) Contributions quadratic in the nonsphericity

To calculate the orientation cross sections quadratic in the nonsphericity one has to start with the corresponding part of the spherical tensor (2.16),

$${}_2\sigma_{KQ}^{(1)}(j_1 j_2, j_1' j_2') = (2j_1+1)^{-1} (2j_2+1)^{-1} (k'/k) \text{tr}_1 \text{tr}_2 [a_1^{j_1 j_2, j_1' j_2'} a_1^{\dagger j_1' j_2', j_1 j_2} T_{KQ}^{j_1 j_2}], \quad (2.24)$$

with a_1 given by Equation (1.26). The left subscript 2 again indicates the order in the nonsphericity. There are, in general, contributions to (2.24) from elastic and inelastic collisions. From Eqs. (1.26), (1.33),

(2.24) and with the use of Racah algebra one finds

$${}_2\sigma_{KQ}^{(1)}(j_1 j_2, j_1' j_2') = \frac{4\pi m^2 k'}{\hbar^4 k} \sum_{LL_1} \sum'_{l'l_1} (j_1 0, l 0 | j_1' 0) (j_1 0, l_1 0 | j_1' 0) (j_2 0, l' 0 | j_2' 0)^2 \\ \mathcal{W}(j_1 j_1 l l_1; K j_1') \sum_{\substack{\lambda\lambda', r, r' \\ \lambda\lambda', l_1\lambda_1'}} C \left(\begin{smallmatrix} l'l'L\lambda\lambda' \\ l_1'l_1L_1\lambda_1\lambda_1' \end{smallmatrix} \right) V_{\lambda\lambda'}^{l'l'L} V_{\lambda_1\lambda_1'}^{l_1'l_1'L_1*} \sum_{qq'} (r q, r' q' | K Q) Y_{rq}(\mathbf{e}) Y_{r'q'}(\mathbf{e}'). \quad (2.25)$$

Here, a more complicated geometry coefficient appears:

$$C \left(\begin{smallmatrix} l'l'L\lambda\lambda' \\ l_1'l_1L_1\lambda_1\lambda_1' \end{smallmatrix} \right) = (-1)^{K-L_1+(\lambda'-\lambda+\lambda_1-\lambda_1')/2} (2\lambda+1)(2\lambda'+1)(2\lambda_1+1)(2\lambda_1'+1)(l 0, l' 0 | L 0) \\ (l_1 0, l'_1 0 | L_1 0) \mathcal{W}(l l_1 L L_1; K l') (\lambda 0, \lambda' 0 | L 0) (\lambda_1 0, \lambda_1' 0 | L_1 0) (\lambda 0, \lambda_1 0 | r 0) (\lambda' 0, \lambda_1' 0 | r' 0) \left\{ \begin{smallmatrix} \lambda\lambda', r \\ l'l', r' \end{smallmatrix} \right\}_{LL_1K},$$

where $\left\{ \begin{smallmatrix} \lambda\lambda', r \\ l'l', r' \end{smallmatrix} \right\}_{LL_1K}$ is a 9 j -symbol¹³.

First the case $K=1$ is considered. From Eqs. (2.25), (2.12) the part of the orientation cross section of the vector polarization quadratic in the nonsphericity is obtained as

$$2\pi \int_0^\pi {}_2\sigma_n^{(1)} \sin \vartheta d\vartheta = \frac{4\pi \sqrt{2} m^2 k'}{3 \hbar^4 k} \sqrt{2j_1+1} g_0(j_1) \sum_{LL_1} \sum'_{l'l_1} (j_1 0, l 0 | j_1' 0) (j_1 0, l_1 0 | j_1' 0) \\ \mathcal{W}(j_1 j_1 l l_1; 1 j_1') (j_2 0, l' 0 | j_2' 0)^2 \sum_{\lambda\lambda', l_1\lambda_1'} C \left(\begin{smallmatrix} l'l'L\lambda\lambda' \\ l_1'l_1L_1\lambda_1\lambda_1' \end{smallmatrix} \right) \text{Im}[V_{\lambda\lambda'}^{l'l'L} V_{\lambda_1\lambda_1'}^{l_1'l_1'L_1*}]. \quad (2.27)$$

To obtain (2.27) use has also been made of the antisymmetry of the coefficient (2.26) for $k=1$ in interchanges $\lambda\lambda' l l \longleftrightarrow \lambda_1\lambda_1' l_1 L_1$. Since (2.26) is antisymmetric also in $\lambda\lambda_1 r \longleftrightarrow \lambda'\lambda_1' r$ but in the elastic case ($k'=k$) $V_{\lambda\lambda'}$ is symmetric, the cross section (2.27) vanishes for elastic collisions. Thus also quadratic in the nonsphericity elastic collisions do not contribute to the orientation cross section of the vector polarization.

Next the case $K=2$ is considered which yields the orientation cross sections of the tensor polarization. From Eqs. (2.10), (2.11), (2.13), (2.14) and (2.25) the following total cross sections are found:

$$2\pi \int_0^\pi {}_2\sigma_{ee}^{(1)} \sin \vartheta d\vartheta = \frac{4\pi m^2 k'}{\hbar^4 k} \sqrt{\frac{10}{3}} \sqrt{2j_1+1} g_1(j_1) \sum_{LL_1} \sum'_{l'l_1} (j_1 0, l 0 | j_1' 0) (j_1 0, l_1 0 | j_1' 0) \\ \mathcal{W}(j_1 j_1 l l_1; 2 j_1') (j_2 0, l' 0 | j_2' 0)^2 \sum_{\lambda\lambda', l_1\lambda_1'} C \left(\begin{smallmatrix} l'l'L\lambda\lambda' \\ l_1'l_1L_1\lambda_1\lambda_1' \end{smallmatrix} \right) \text{Re}[V_{\lambda\lambda'}^{l'l'L} V_{\lambda_1\lambda_1'}^{l_1'l_1'L_1*}], \quad (2.28)$$

and

$$2\pi \int_0^\pi {}_2\sigma_{e'e'}^{(1)} \sin \vartheta d\vartheta = \frac{20\pi m^2 k'}{3 \hbar^4 k} \sqrt{2j_1+1} g_1(j_1) \sum_{LL_1} \sum'_{l'l_1} (j_1 0, l 0 | j_1' 0) (j_1 0, l_1 0 | j_1' 0) \\ \cdot \mathcal{W}(j_1 j_1 l l_1; 2 j_1') (j_2 0, l' 0 | j_2' 0)^2 \sum_{\lambda\lambda', l_1\lambda_1'} C \left(\begin{smallmatrix} l'l'L\lambda\lambda' \\ l_1'l_1L_1\lambda_1\lambda_1' \end{smallmatrix} \right) \text{Re}[V_{\lambda\lambda'}^{l'l'L} V_{\lambda_1\lambda_1'}^{l_1'l_1'L_1*}]. \quad (2.29)$$

The orientation cross section ${}_2\sigma_{e'e'}^{(1)}$ needs not to be treated separately since from Eqs. (2.14), (2.25) and the symmetry of (2.26) in primed and unprimed λ 's and r 's for $k=2$ the symmetry relation

$$k^2 {}_2\sigma_{e'e'}^{(1)}(k, k') = k'^2 {}_2\sigma_{ee}^{(1)}(k', k) \quad (2.30)$$

can be derived. Here, the notation $\sigma_{ee}(k', k)$ indicates that the sequence of arguments in $V_{\lambda\lambda'}$, $V_{\lambda_1\lambda_1'}$ is (k', k) instead of (k, k') (which is tacitly understood if the arguments are missing). Because of (2.30) for elastic collisions also quadratic in the nonsphericity the relation

$${}_2\sigma_{e'e'}^{(1)} = {}_2\sigma_{ee}^{(1)}$$

holds. This implies that within the first order DWBA treatment only inelastic collisions contribute to the effective coupling cross section of friction pressure and tensor polarization, $\sigma^{n,T}$ [Equation (I 3.44)].

For later application to the HD-HD interaction finally an explicit expression for the total cross section (2.28) due to a P_1 -potential of the form (1.6) is given [$l=l_1=L=L_1=1, l'=0$ in (2.28)]

$$2\pi \int_0^\pi \sin \vartheta d\vartheta = -\frac{4\pi m^2 k'}{3\hbar^4 k} \sqrt{2j_1+1} g_1(j_1) (j_1 0, 10 | j_1' 0)^2 W(j_1 j_1 11; 2 j_1') \delta_{j_1 j_1'} \quad (2.31)$$

$$\sum_{\lambda=0}^{\infty} (\lambda+1)(\lambda+2) \{ (2\lambda+1)^{-1} |V_{\lambda+1\lambda}^{101}|^2 + (2\lambda+5)^{-1} |V_{\lambda+1\lambda+2}^{101}|^2 - 6(2\lambda+3)^{-1} \text{Re}[V_{\lambda\lambda+1}^{101} V_{\lambda+2\lambda+1}^{101*}] \}.$$

Equation (2.31) is appropriate for further numerical evaluation.

3. Reorientation Cross Sections for \mathbf{J} -Multipolarizations

Reorientation cross sections determine the relaxation coefficients of rotational angular momentum multipolarizations, e.g. σ^T , the effective relaxation cross section of the tensor polarization important for a lot of nonequilibrium alignment phenomena¹. In I two kinds of molecular reorientation cross sections have been introduced – both vanishing for a spherical potential – namely

$$\text{re}\sigma_K^{(1)} = \frac{(2K+1)!!}{K!} (2j_1+1)^{-1} (2j_2+1)^{-1} \frac{k'}{k} \text{tr}_1 \text{tr}_2 [\overline{J_{1\mu_1} \dots J_{1\mu_K}} a^{j_1 j_2, j_1' j_2'} [a^\dagger, \overline{J_{1\mu_1} \dots J_{1\mu_K}}] \underline{j_1' j_2', j_1 j_2}], \quad (2.32)$$

$$\text{re}\sigma_K^{(2)} = \frac{(2K+1)!!}{K!} (2j_1+1)^{-1} (2j_2+1)^{-1} \frac{k'}{k} \text{tr}_1 \text{tr}_2 [\overline{J_{1\mu_1} \dots J_{1\mu_K}} a^{j_1 j_2, j_1' j_2'} [a^\dagger, \overline{J_{2\mu_1} \dots J_{2\mu_K}}] \underline{j_1' j_2', j_1 j_2}]. \quad (2.33)$$

As can be seen from inspection of the traces, only the “nonspherical” part a_1 of the scattering amplitude contributes to (2.32), (2.33). The reorientation cross sections are thus of second order in the nonsphericity. For further evaluation of (2.32), (2.33) the following identity for scalar products of K^{th} rank irreducible angular momentum tensors is used:

$$\begin{aligned} \frac{(2K+1)!!}{K!} P^{j_1} \overline{J_{\mu_1} \dots J_{\mu_K}} P^{j_1} [\dots]^{j_1 j_2, j_1' j_2'} P^{j_1'} \overline{J_{\mu_1} \dots J_{\mu_K}} P^{j_1'} \\ = \sqrt{(2j_1+1)(2j_1'+1)} g_{K-1}(j_1) g_{K-1}(j_1') \sum_Q T_{KQ}^{j_1 j_2} [\dots]^{j_1 j_2, j_1' j_2'} T_{KQ}^{j_1' j_2'} \end{aligned} \quad (2.34)$$

A similar relation is valid if j_1' is replaced by j_2' . The bracket in (2.34) may contain any operator acting in rotational angular momentum space.

From Eqs. (1.26), (1.33), (2.32) and (2.34) the total reorientation cross section of the K^{th} rank tensor polarization is obtained:

$$\begin{aligned} 2\pi \int_0^\pi \text{re}\sigma_K^{(1)} \sin \vartheta d\vartheta = \frac{4\pi m^2 (2K+1)k'}{\hbar^4 k} \sum_L \sum_{l'} B_{j_1 j_1'}^{lK} (j_2 0, l' 0 | j_2' 0)^2 \\ [(2l+1)(2l'+1)(2L+1)]^{-1} (l 0, l' 0 | L 0)^2 \sum_{\lambda \lambda'} (2\lambda+1)(2\lambda'+1) (\lambda 0, \lambda' 0 | L 0)^2 |V_{\lambda \lambda'}^{lL}|^2. \end{aligned} \quad (2.35)$$

Here, the coefficient $B_{j_1 j_1'}^{lK}$ is given by

$$B_{j_1 j_1'}^{lK} = g_{K-1}(j_1) (j_1 0, l 0 | j_1' 0)^2 [g_{K-1}(j_1) - (-1)^K g_{K-1}(j_1')] \sqrt{(2j_1+1)(2j_1'+1)} W(j_1 j_1 j_1' j_1'; K l). \quad (2.36)$$

From a property of the Racah coefficient follows that this coefficient vanishes for $l=0$ or $K=0$. Analogously we find for the reorientation cross section (2.33) integrated over the solid angle the expression

$$\begin{aligned} 2\pi \int_0^\pi \text{re}\sigma_K^{(2)} \sin \vartheta d\vartheta = \frac{4\pi m^2 k'}{\hbar^4 k} \sum_L \sum_{l, l'} \sum_{l_1, l_1'} C_{j_1 j_1'}^{l, l_1, K} \tilde{C}_{j_1 j_1'}^{l, l_1', K} (2l+1)^{-1} (2l'+1)^{-1} \\ (2L+1)^{-1} (l 0, l' 0 | L 0) (l_1 0, l_1' 0 | L 0) \sum_{\lambda \lambda'} (2\lambda+1)(2\lambda'+1) (\lambda 0, \lambda' 0 | L 0)^2 \text{Re}(V_{\lambda \lambda'}^{lL} V_{\lambda \lambda'}^{l_1 l_1' L*}) \end{aligned} \quad (2.37)$$

with

$$C_{j_1 j_1'}^{l l' K} = \sqrt{2 j_1 + 1} g_{K-1}(j_1) (j_1 0, l 0 | j_1' 0) (j_1 0, l_1 0 | j_1' 0) \mathcal{W}(l l_1 j_1 j_1'; K j_1') \quad (2.38 a)$$

and

$$\begin{aligned} \tilde{C}_{j_2 j_2'}^{l' l'_1 K} = & (j_2 0, l' 0 | j_2' 0) (j_2 0, l'_1 0 | j_2' 0) [\sqrt{2 j_2 + 1} g_{K-1}(j_2) \mathcal{W}(l' l'_1 j_2 j_2'; K j_2') \\ & - (-1)^K \sqrt{2 j_2' + 1} g_{K-1}(j_2') \mathcal{W}(l' l'_1 j_2' j_2'; K j_2')] . \end{aligned} \quad (2.38 b)$$

For collisions with $j_2 = j_2'$, e. g. elastic scattering, the coefficient $\tilde{C}_{j_2 j_2'}^{l' l'_1 K}$ and thus $\sigma_K^{(2)}$ vanish for even K values.

The important special case of a pure P_L -potential, Eq. (1.6), is obtained if in (2.35) and (2.37) only the terms $l = l_1 = L$, $l' = l'_1 = 0$ and $l' = l'_1 = L$, $l = l_1 = 0$ are retained. Then Eqs. (2.35) and (2.37) reduce to

$$2 \pi \int_0^\pi \sigma_K^{(1)} \sin \vartheta d\vartheta = \frac{4 \pi m^2 k'}{\hbar^4 k} \frac{2 K + 1}{(2 L + 1)^2} B_{j_1 j_1'}^{LK} \delta_{j_2 j_2'} \sum_{\lambda \lambda'} (2 \lambda + 1) (2 \lambda' + 1) (\lambda 0, \lambda' 0 | L 0)^2 |V_{\lambda \lambda'}^{L0L}|^2, \quad (2.39)$$

and

$$2 \pi \int_0^\pi \sigma_K^{(2)} \sin \vartheta d\vartheta = 0. \quad (2.40)$$

For later application to the calculation of σ^T for the HD-HD interaction, we need the total reorientation cross section of the tensor polarization due to a $P_1(\mathbf{u}_1 \cdot \hat{\mathbf{r}})$ -potential:

$$\begin{aligned} 2 \pi \int_0^\pi \sigma_K^{(1)} \sin \vartheta d\vartheta = & 15 g_1(j_1) (j_1 0, 10 | j_1' 0)^2 \delta_{j_2 j_2'} \\ & [g_1(j_1) - g_1(j_1')] \sqrt{(2 j_1 + 1)(2 j_1' + 1)} \mathcal{W}(j_1 j_1 j_1' j_1'; 21) \sum_{\lambda} (\lambda + 1) (|V_{\lambda \lambda+1}^{101}|^2 + |V_{\lambda+1 \lambda}^{101}|^2). \end{aligned} \quad (2.41)$$

The r.h.s. of (2.41) is seen to be proportional to the total cross section $2 \pi \int_0^\pi \sigma_1 \sin \vartheta d\vartheta$ [Equations (2.6), (2.7)].

As a simple application of Eq. (2.39) to single level (j) systems interacting via a potential (1.6) with $L = 2$ are considered. After insertion of explicit expressions for the ensuing Clebsch-Gordan and Racah-coefficients the following ratio of the effective reorientation cross sections of vector- and tensor polarization, σ^V and σ^T , is found:

$$\sigma^V / \sigma^T = 5 \sigma_1^{(1)} / 3 \sigma_2^{(1)} = [4 j(j+1) - 3] / 3 [4 j(j+1) - 7]. \quad (2.42)$$

Equation (2.42) is important for the theory of nuclear spin relaxation in H_2 and agrees with a formula obtained by Bloom et al.¹⁵ with different methods. In particular, for o- H_2 in the ground state ($j = 1$) one has $\sigma^V / \sigma^T = 5/3$.

In I, also more general orientation and reorientation cross sections have been introduced. They are not treated here since they play a role only if the nonsphericity is no longer small. Then the present DWBA treatment would no more be valid.

III. Application: Calculation of the Effective Cross Sections σ^T and $\sigma^{\eta, T}$ for HD (HT) at Room Temperature

In this section, two important Waldmann-Snider collision integrals are calculated for HD (HT) at room temperature, namely the relaxation cross section of the tensor polarization, σ^T , and the coupling cross section of friction pressure tensor and tensor polarization, $\sigma^{\eta, T} = \sigma^{T, \eta}$. In I we derived the expressions

$$\begin{aligned} \sigma^T = & \frac{4 \pi}{5} \langle J^2(J^2 - \frac{3}{4}) \rangle_0^{-1} Q^{-2} \sum_{j_1 j_2 j_1' j_2'} (2 j_1 + 1) (2 j_2 + 1) \exp \{ -\gamma^2 - \varepsilon(j_1) - \varepsilon(j_2) \} \\ & \gamma^3 (\sigma_2^{(1)} + \sigma_2^{(2)}) \sin \vartheta d\vartheta d\gamma, \end{aligned} \quad (3.1) \quad \text{and (I.3.28)}$$

$$\sigma^{\eta,T} = \frac{4\pi\sqrt{2}}{5} \langle J^2(J^2 - \frac{3}{2}) \rangle_0^{-1/2} Q^{-2} \sum_{j_1 j_2 j_1' j_2'} \int \int (2j_1 + 1)(2j_2 + 1) \exp\{-\gamma^2 - \varepsilon(j_1) - \varepsilon(j_2)\} \\ \cdot \gamma^3 (\gamma^2 \sigma_{ee}^{(1)} - \gamma'^2 \sigma_{e'e'}^{(1)}) \sin \vartheta d\vartheta d\gamma. \quad (3.2) \quad \text{and (I.3.44)}$$

In (3.1), (3.2), the symbol $\langle \dots \rangle_0$ denotes an equilibrium average, Q is the rotational partition sum and

$$\gamma = \hbar k / m k_B T_0, \quad \varepsilon(j) = E(j) / k_B T_0$$

are the dimensionless relative velocity after the collision and the dimensionless rotational energy, respectively. The γ -integration has to be performed such that always γ^2 and $\gamma'^2 = \gamma^2 + \Delta\varepsilon$ are positive. The molecular cross sections occurring in (3.1) and (3.2) have been defined by Eqs. (2.10), (2.11), (2.32), (2.33). DWBA-expressions for the corresponding total cross sections (molecular cross sections integrated over the solid angle $2\pi \sin \vartheta d\vartheta$) have been given in the preceding section. They depend on the radial integrals $V_{\lambda\lambda'}^{ll'L}(k, k')$ defined by Eq. (1.34). In the following, these radial integrals are evaluated within a simple interaction model for HD (HT) molecules.

1. Interaction Model and Scattering Amplitude for Asymmetric Molecules

A simple model of a nonspherical interaction is studied for diatomic molecules whose centers of mass do not coincide with the geometric centers (e. g. HD, HT). It takes into account only the repulsive part of the potential and may thus be used for calculations of collision integrals for high enough temperature when the attractive interaction should play a minor role. The model, however, permits the analytical calculation of the distorted waves and the corresponding radial integrals Equation (1.34). This is desirable since the summations over rotational quantum numbers and orbital angular mo-

menta as well as the γ -integration can, anyhow, only be performed numerically.

Starting point for our model is a spherical potential between the corresponding homonuclear molecules (e. g. H_2). This potential is assumed as

$$V_0(r) = U_0 \Theta(r_0 - r), \quad (3.3)$$

where $U_0 > 0$ and r_0 is the molecular diameter; the Heaviside step function is denoted by Θ . The nonsphericity of the homonuclear molecules is neglected. This is a good approximation for H_2 , D_2 molecules. After Eq. (1.7), the nonspherical interaction between the asymmetric molecules linear in the small excentricity d is

$$V(\mathbf{u}_1, \mathbf{u}_2, \mathbf{r}) = V_0(r) + V_1(r) [P_1(\mathbf{u}_1 \cdot \hat{\mathbf{r}}) - P_1(\mathbf{u}_2 \cdot \hat{\mathbf{r}})] \quad (3.4)$$

with

$$V_1(r) = -U_0 d \delta(r - r_0). \quad (3.5)$$

The average nonsphericity parameter $\bar{\varepsilon}$ is then

$$\bar{\varepsilon} = \left| \int_0^\infty V_1 dr / \int_0^\infty V_0 dr \right| = |d/r_0| (\ll 1 \text{ for HD}).$$

After performance of all ensuing calculations for finite U_0 the hard sphere limit $U_0 \rightarrow \infty$ is taken. Our model can thus be understood as the quantum mechanical analogue to the classical model of rigid loaded spheres¹⁶.

The radial Schrödinger Eq. (1.31) obeying the boundary condition (1.3) can easily be solved for the spherical potential Equation (3.3). From the regularity of the wave function at the origin and continuity of the function and its derivative at $r = r_0$ we obtain the radial part of the distorted waves:

$$\chi_\lambda^{(+)}(k, r) = \begin{cases} B_\lambda j_\lambda(\kappa r), & r < r_0 \\ j_\lambda(kr) + [B_\lambda j_\lambda(\kappa r_0) - j_\lambda(kr_0)] h_\lambda^{(1)}(kr) / h_\lambda^{(1)}(kr_0), & r > r_0. \end{cases} \quad (3.6)$$

In (3.6) one has

$$B_\lambda = \frac{-i}{k r_0^2} [\kappa j_\lambda'(\kappa r_0) h_\lambda^{(1)}(kr_0) - k j_\lambda(\kappa r_0) h_\lambda^{(1)'}(kr_0)]^{-1}, \quad (3.7)$$

$$\kappa^2 = k^2 - m U_0 / \hbar^2. \quad (3.8)$$

In Eqs. (3.6), (3.7), j_λ and $h_\lambda^{(1)}$ are spherical Bessel- and Hankel functions of the first kind as defined

in the text of Abramowitz and Stegun¹⁷. The prime in Eq. (3.7) denotes the derivative with respect to the argument. Using Eqs. (3.5) – (3.8) we can im-

mediately evaluate the radial integrals $V_{\lambda\lambda'}^{101}(k, k')$ and perform the hard sphere limit $U_0 \rightarrow \infty$:

$$\lim_{U_0 \rightarrow \infty} V_{\lambda\lambda'}^{101}(k, k') = \frac{\hbar^2 d}{m r_0^2 k k'} [h_\lambda^{(1)}(k r_0) h_{\lambda'}^{(1)}(k' r_0)]^{-1}. \quad (3.9)$$

It should be stressed that (3.9) contains no adjustable parameter. The excentricity d is determined by the atomic masses and by the equilibrium distance of the atoms in the molecules according to Equation (1.8). The diameter r_0 can be taken from the viscosity cross section for classical hard spheres

$$\sigma^\eta = \frac{4\pi}{5} r_0^2.$$

The function $1/h_\lambda^{(1)}(x)$ remains finite for $x=0$ and has no singularities for $x>0$. For large λ -values it has the asymptotic form

$$1/h_\lambda^{(1)}(x) \sim i \sqrt{\frac{e}{2}} \left(\frac{e}{2\lambda+1} \right)^\lambda x^{\lambda+1},$$

$$\begin{aligned} \sum_{j_1 j_2 j_1' j_2'} \int_{\gamma, \gamma' \geq 0}^\infty d\gamma \exp\{-\gamma^2 - \varepsilon(j_1) - \varepsilon(j_2)\} \gamma^2 \gamma' F(j_1 j_2, j_1' j_2'; \gamma, \gamma') \\ = \sum_{j_1 j_2 j_1' j_2'} \int_{\Delta\varepsilon > 0}^\infty d\gamma \exp\{-\gamma^2 - \varepsilon(j_1) - \varepsilon(j_2)\} \gamma^2 \gamma' [F(j_1 j_2, j_1' j_2'; \gamma, \gamma') + F(j_1' j_2', j_1 j_2; \gamma', \gamma)]. \end{aligned} \quad (3.11)$$

Since after Eqs. (2.31) and (2.41) the ensuing cross sections are proportional to $\delta_{j_1 j_2'} (re\sigma_2^{(2)} = 0)$, only F 's of the form

$F(j_1 j_2, j_1' j_2'; \gamma, \gamma') = (2j_2 + 1) \delta_{j_1 j_2'} F(j_1 j_1'; \gamma, \gamma')$ appear after Eqs. (3.1), (3.2). The sum over j_2, j_2' thus merely gives Q , the rotational partition sum. Because of $\Delta\varepsilon > 0$ only

$$j_1 = j_1' + 1, \quad \Delta\varepsilon = \varepsilon(j_1' + 1) - \varepsilon(j_1') \\ = \hbar^2 (j_1' + 1) / k_B T_0 \Theta$$

have to be taken into account.

For the calculation of σ^T and $\sigma^{\eta, T}$ after Eqs. (3.1), (3.2), Eqs. (2.31), (2.30), (2.41) and (3.9), (3.11) are used. For the numerical γ -integration a Gauss-Hermite procedure is applied. A summation over 10 j_1' -values (rotational angular momenta) and 40 λ -values (orbital angular momenta) and the choice of 5 abscissas for the Gaussian method proved to be sufficient to obtain an accuracy of the calculated σ^T and $\sigma^{\eta, T}$ -values better than 1%. The molecular diameter r_0 (which, in our model, is the same

i. e. for fixed x , the function (3.9) approaches zero rapidly with increasing λ . Thus the λ -summation in the expressions for the total cross sections may be truncated at a finite λ_{\max} with only small error. It should be mentioned here that Gioumousis and Curtiss¹⁸ obtained similar results for the scattering amplitude of "nearly spherical rigid bodies" but with quite a different method and aim.

2. Calculation of σ^T and $\sigma^{\eta, T}$ for HD (HT) at Room Temperature

For HD-molecules with the interaction potential (3.4) the selection rule (1.27) yields

$$j_1 = j_1' \pm 1, \quad (3.10)$$

and the same for j_2 . Thus only inelastic collisions contribute to the total cross sections and the energy transfer $\Delta\varepsilon$ may be positive and negative. But with the help of $\gamma d\gamma = \gamma' d\gamma'$ and the energy conservation (1.23 a) the following equality, valid for any function $F(j_1 j_2, j_1' j_2'; \gamma, \gamma')$ can be derived:

for H_2 , HD, HT) has been taken from the rigid sphere viscosity cross section at room temperature¹². The excentricity d has been inferred from Eq. (1.8) where the equilibrium distance of the atoms in the H_2 molecule $b = 0.74 \text{ \AA}$ has been used. The rotational temperature $T_{\text{rot}} = \hbar^2 / 2 k_B \Theta$ has been taken from the literature¹⁹. The constants used are summarized in the following table:

	HD	HT
r_0 in \AA	2.72	2.72
d in \AA	0.1233	0.185
T_{rot} in K	64	57

The next table shows the theoretical results for σ^T and $\sigma^{\eta, T}$ for HD at 293 K. They are compared with experimental values taken from measurements by Hulsman et al.⁵ on the transverse Senftleben-Beenakker effect of the viscosity and, for σ^T , also from measurements of the depolarized Rayleigh line by Gupta⁶. These results have already been reported in a letter²⁰.

	Theor. Value	Exp. Value
σ^T in \AA^2	2.58	Hulsman 1970: 2.3 ± 0.07 Gupta 1971: 2.73 ± 0.14
$\sigma^{\eta, T}$ in \AA^2	0.55	Hulsman 1970: $\pm (0.29 \pm 0.015)$

For HT one finds the theoretical values: $\sigma^T = 7.01 \text{\AA}^2$ and $\sigma^{\eta, T} = 1.50 \text{\AA}^2$ but there are no measurements to compare with. The agreement is good for σ^T ; the calculated "nondiagonal" collision integral $\sigma^{\eta, T}$ is too large.

The simple interaction model could be amended by adding an attractive square well to the repulsive

core. The DWBA scattering amplitude could then still be evaluated analytically. But now two adjustable parameters (depth and range of the well) would appear. Hopefully, a better value for $\sigma^{\eta, T}$ could be found and also the temperature dependence of the collision integrals in the experimental range of 50 – 300 K could be investigated.

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Appendix A

Properties of the Spherical Tensor Operators $T_{lm}^{jj'}$

Some properties of the spherical tensor operators in rotational angular momentum space

$$T_{lm}^{jj'} = \sum_{m''} (-1)^{j-m''} (j' m', j-m'' | l m) | j m'' \rangle \langle j' m' | \quad (1.26)$$

are listed:

a) Adjoint operator

$$T_{lm}^{†jj'} \equiv [T_{lm}^{jj'}]^\dagger = (-1)^{j-j'+m} T_{l-m}^{jj'} \quad (A 1)$$

b) Trace property

$$\text{tr} \{ T_{lm}^{jj'} [T_{l'm'}^{jj'}]^\dagger \} = \delta_{ll'} \delta_{mm'} \quad (A 2)$$

c) Coupling of two tensor operators

$$T_{lm}^{jj'} T_{l'm'}^{j''j'} = \sum_{kq} \sqrt{(2l+1)(2l'+1)} W(j l j' l'; j'' k) (l m, l' m' | k q) T_{kq}^{jj'} \quad (A 3)$$

where $W(\dots)$ is a Racah coefficient.

d) Scalar product

$$\sum_m T_{lm}^{jj'} [T_{lm}^{jj'}]^\dagger = \frac{2l+1}{2j+1} P^j \quad (A 4)$$

where P^j is the projection operator into the j -subspace.

e) Scalar product – trace-relation

$$\sum_q \text{tr} \{ T_{kq}^{jj} T_{lm}^{jj'} [T_{kq}^{jj'}]^\dagger [T_{l'm'}^{jj'}]^\dagger \} = (-1)^{l+k-j-j'} (2k+1) W(j j j' j'; k l) \delta_{ll'} \delta_{mm'} \quad (A 5)$$

Appendix B

Differential Cross Sections

The total cross sections relevant for the most important Waldmann-Snider collision integrals have been studied in Sect. II of this paper. Here, the underlying differential cross sections are considered. They are presented as Legendre-polynomial series $\sum_R a_R P_R(\cos \vartheta)$ where ϑ is the angle of deflection. Starting points are, in any case, the Eqs. (1.26), (1.29) and (1.33). To obtain the desired expressions, extensive use is made of Racah techniques. The cross sections are written such as to distinguish clearly between collision geometry (geometry coefficients and Legendre polynomials) and collision dynamics (radial matrix elements).

1) Scattering cross section

The Legendre-polynomial series for the cross section due to a spherical potential, σ_0 , is well known⁴. The differential cross section σ_1 [Eq. (2.3 b)] due to the nonspherical part of the interaction is obtained as

$$\sigma_1(j_1 j_2, j_1' j_2'; k, \vartheta) = \frac{m^2 k'}{\hbar^4 k} \sum_R \left\{ \sum_L \sum_{l'} (j_1 0, l 0 | j_1' 0)^2 (j_2 0, l' 0 | j_2' 0)^2 \sum_{\lambda \lambda' \lambda_1 \lambda_1'} A_{\lambda \lambda' \lambda_1 \lambda_1'}^{ll'LR} \operatorname{Re}[V_{\lambda \lambda'}^{ll'L}(k, k') V_{\lambda_1 \lambda_1'}^{ll'L}(k, k')^*] \right\} P_R(\cos \vartheta). \quad (\text{B } 1)$$

The geometry coefficient $A_{\lambda \lambda' \lambda_1 \lambda_1'}^{ll'LR}$ has already been explained by Equation (2.4). It is the special case $l_1 = l, l_1' = l'$ of a more general coefficient $A_{\lambda \lambda' \lambda_1 \lambda_1'}^{ll' l_1 l_1' L}$ to appear later:

$$A_{\lambda \lambda' \lambda_1 \lambda_1'}^{ll' l_1 l_1' L} = [(2l+1)(2l'+1)(2L+1)]^{-1} (l 0, l' 0 | L 0) (l_1 0, l_1' 0 | L 0) (\lambda 0, \lambda' 0 | L 0) (\lambda_1 0, \lambda_1' 0 | L 0) (\lambda 0, \lambda_1 0 | R 0) (\lambda' 0, \lambda_1' 0 | R 0) (-1)^{(2\lambda+2\lambda'+2\lambda_1+2\lambda_1')/2} (2\lambda+1)(2\lambda'+1)(2\lambda_1+1)(2\lambda_1'+1) \mathcal{W}(\lambda \lambda_1 \lambda' \lambda_1'; R L). \quad (\text{B } 2)$$

2) Orientation cross sections for vector- and tensor polarization

a) Contributions linear in the nonsphericity

The part linear in the nonsphericity of the orientation cross section of the vector polarization, ${}_1\sigma_n^{(1)}$, vanishes [cf. Eq. (2.20)]. For the corresponding differential orientation cross sections for the tensor polarization, ${}_1\sigma_{ee}^{(1)}$, ${}_1\sigma_{e'e'}^{(1)}$, and ${}_1\sigma_{ee'}^{(1)}$ one finds with the help of Eqs. (2.10), (2.12) – (2.14), (2.18) and (2.19):

$${}_1\sigma_{ee}^{(1)}(j_1 j_2; k, \vartheta) = {}_1\sigma_{e'e'}^{(1)}(j_1 j_2; k, \vartheta) = \frac{1}{5} \sqrt{\frac{2}{3}} \frac{m}{\hbar^2 k} j_1(j_1+1) \sum_R \left\{ \sum_{\lambda \lambda' \lambda_2} B_{\lambda \lambda' \lambda_2 R} \operatorname{Re}[e^{-i\delta_{\lambda 2}(k)} \sin \delta_{\lambda_2}(k) V_{\lambda \lambda'}^{202}(k)] \right\} P_R(\cos \vartheta),$$

$${}_1\sigma_{ee'}^{(1)}(j_1 j_2; k, \vartheta) = \frac{1}{\sqrt{5}} \frac{m}{\hbar^2 k} j_1(j_1+1) \sum_R \left\{ \sum_{\lambda \lambda' \lambda_2} B'_{\lambda \lambda' \lambda_2 R} \operatorname{Re}[e^{-i\delta_{\lambda 2}(k)} \sin \delta_{\lambda_2}(k) V_{\lambda \lambda'}^{202}(k)] \right\} \cdot P_R(\cos \vartheta). \quad (\text{B } 4)$$

In (B 3) and (B 4) the geometry coefficients

$$B_{\lambda \lambda' \lambda_2 R} = \sum_{\lambda_1} B_{\lambda \lambda' \lambda_1 R 2 \lambda_2} (-1)^{\lambda_1} \sqrt{(2R+1)(2\lambda_1+1)} (\lambda_1 0, 20 | R 0), \quad (\text{B } 5)$$

$$B'_{\lambda \lambda' \lambda_2 R} = (-1)^R \sum_{\lambda_1 \lambda_1'} B_{\lambda \lambda' \lambda_1 \lambda_1' 2 \lambda_2} \sqrt{(2\lambda_1+1)(2\lambda_1'+1)} (\lambda_1 0, 10 | R 0) (\lambda_1' 0, 10 | R 0) \mathcal{W}(\lambda_1 1 \lambda_1' 1; R 2) \quad (\text{B } 6)$$

appear. The coefficient $B_{\lambda \lambda' \lambda_1 R 2 \lambda_2}$ has been defined by Equation (2.19).

b) Contributions quadratic in the nonsphericity

Starting point for the calculation of the orientation cross sections quadratic in the nonsphericity is Equation (2.25). With the help of Eq. (2.12) the orientation cross section of the vector polarization is obtained as

$${}_2\sigma_n^{(1)}(j_1 j_2, j_1' j_2'; k, \vartheta) \sin \vartheta = \frac{3\sqrt{2} m^2 k'}{\hbar^4 k} \sqrt{(2j_1+1)} g_0(j_1) \sum_R \left\{ \sum_{L L_1} \sum_{l' l_1} (j_1 0, l 0 | j_1' 0) (j_1 0, l_1 0 | j_1' 0) \mathcal{W}(j_1 j_1 l l_1; 1 j_1') (j_2 0, l' 0 | j_2' 0)^2 \sum_{\lambda \lambda' \lambda_1 \lambda_1'} D_{\lambda \lambda' \lambda_1 \lambda_1' R 1}^{ll' L L_1 L_1} \operatorname{Im}[V_{\lambda \lambda'}^{ll'L}(k, k') V_{\lambda_1 \lambda_1'}^{l_1 l_1' L_1}(k, k')^*] \right\} P_R(\cos \vartheta). \quad (\text{B } 7)$$

The D -coefficient occurring in (B 7) is the special case $K=1$ of the geometry coefficient

$$D_{\lambda \lambda' \lambda_1 \lambda_1' R K}^{ll' L L_1 L_1} = (-1)^{R+K} \sum_{r, r'} C_{\lambda \lambda' \lambda_1 \lambda_1' R K}^{ll' L L_1 L_1} \sqrt{(2r+1)(2r'+1)} (r 0, 10 | R 0) (r' 0, 10 | R 0) \mathcal{W}(r r' 11; K R), \quad (\text{B } 8)$$

where the C -coefficient has been explained by Equation (2.26). With the help of Eq. (2.14) the orientation cross section of the tensor polarization ${}_2\sigma_{ee'}^{(1)}$ is found to be

$${}_2\sigma_{ee'}^{(1)}(j_1 j_2, j_1' j_2'; k, \vartheta) = \frac{5 m^2 k'}{\hbar^4 k} \sqrt{(2 j_1 + 1)} g_1(j_1) \sum_R \left\{ \sum_{LL_1} \sum_{l'l_1} (j_1 0, l 0 | j_1' 0) (j_1 0, l_1 0 | j_1' 0) \right. \\ \left. W(j_1 j_1 l l_1; 2 j_1') (j_2 0, l' 0 | j_2' 0)^2 \sum_{\lambda\lambda' \lambda_1 \lambda_1'} D_{\lambda\lambda' \lambda_1 \lambda_1'}^{l'l' L_1 L_1} \operatorname{Re} [V_{\lambda\lambda'}^{l'l L} (k, k') V_{\lambda_1 \lambda_1'}^{l_1 l_1' L_1} (k, k')^*] \right\} P_R(\cos \vartheta). \quad (\text{B } 9)$$

By use of Eq. (2.13) one obtains the cross section ${}_2\sigma_{ee}^{(1)}$ as

$${}_2\sigma_{ee}^{(1)}(j_1 j_2, j_1' j_2'; k, \vartheta) = \sqrt{\frac{2}{3}} \frac{m^2 k'}{\hbar^4 k} \sqrt{2 j_1 + 1} g_1(j_1) \sum_R \left\{ \sum_{LL_1} \sum_{l'l_1} (j_1 0, l 0 | j_1' 0) (j_1 0, l_1 0 | j_1' 0) \right. \\ \left. W(j_1 j_1 l l_1; 2 j_1') (j_2 0, l' 0 | j_2' 0)^2 \sum_{\lambda\lambda' \lambda_1 \lambda_1'} F_{\lambda\lambda' \lambda_1 \lambda_1'}^{l'l' L_1 L_1} \operatorname{Re} [V_{\lambda\lambda'}^{l'l L} (k, k') V_{\lambda_1 \lambda_1'}^{l_1 l_1' L_1} (k, k')^*] \right\} P_R(\cos \vartheta) \quad (\text{B } 10)$$

with

$$F_{\lambda\lambda' \lambda_1 \lambda_1'}^{l'l' L_1 L_1} = \sum_r \sqrt{(2 R + 1) (2 r + 1)} (r 0, R 0 | 20) C_{r R 2}^{(l'l' L_1 L_1 \lambda_1 \lambda_1')}. \quad (\text{B } 11)$$

After Eq. (2.30) the corresponding expression for ${}_2\sigma_{e'e'}^{(1)}$ is obvious.

3) Reorientation cross sections

The differential reorientation cross sections for the K^{th} rank tensor polarization, ${}_{\text{re}}\sigma_K^{(1)}$ and ${}_{\text{re}}\sigma_K^{(2)}$ are calculated according to Equations (2.32) – (2.34). One obtains

$${}_{\text{re}}\sigma_K^{(1)}(j_1 j_2, j_1' j_2'; k, \vartheta) = \frac{m^2 k'}{\hbar^4 k} (2 K + 1) \sum_R \left\{ \sum_L \sum_{l'l'} B_{j_1 j_1'}^{LK} (j_2 0, l' 0 | j_2' 0)^2 \right. \\ \left. \sum_{\lambda\lambda' \lambda_1 \lambda_1'} A_{\lambda\lambda' \lambda_1 \lambda_1'}^{l'l' LR} \operatorname{Re} [V_{\lambda\lambda'}^{l'l L} (k, k') V_{\lambda_1 \lambda_1'}^{l_1 l_1' L} (k, k')^*] \right\} P_R(\cos \vartheta). \quad (\text{B } 12)$$

The coefficients $A_{\lambda\lambda' \lambda_1 \lambda_1'}^{l'l' LR}$ and $B_{j_1 j_1'}^{LK}$ have been defined earlier by Eqs. (2.4) and (2.36), respectively.

Similarly one finds

$${}_{\text{re}}\sigma_K^{(2)}(j_1 j_2, j_1' j_2'; k, \vartheta) = \frac{m^2 k'}{\hbar^4 k} \sum_R \left\{ \sum_{l'l'} \sum_{l_1 l_1'} C_{j_1 j_1'}^{l'l K} \tilde{C}_{j_2 j_2'}^{l_1 l_1' K} \right. \\ \left. \sum_{\lambda\lambda' \lambda_1 \lambda_1'} A_{\lambda\lambda' \lambda_1 \lambda_1'}^{l'l' L_1 L_1} \operatorname{Re} [V_{\lambda\lambda'}^{l'l L} (k, k') V_{\lambda_1 \lambda_1'}^{l_1 l_1' L} (k, k')^*] \right\} P_R(\cos \vartheta). \quad (\text{B } 13)$$

The coefficients $C_{j_1 j_1'}^{l'l K}$ and $\tilde{C}_{j_2 j_2'}^{l_1 l_1' K}$ have been explained by Eqs. (2.38 a, b) and the A -coefficient by Equation (B 2).

While only the corresponding total cross sections are needed for the Waldmann-Snider collision integrals, the differential cross sections may be important for the description of scattering experiments, in particular those where the polarization of the scattered molecules is investigated.

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