

Rotational Angular Momentum Dependence of the Scattering Amplitude for Elastic Molecular Collisions

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The rotational angular momentum (spin) dependence of the binary scattering amplitude operator is investigated for elastic collisions of homonuclear diatomic molecules with monatomic and diatomic particles. Starting point is a formal expansion of the T -matrix (and consequently of the scattering amplitude) with respect to the nonsphericity parameter ε which essentially measures the ratio of the nonspherical and spherical parts of the interaction potential. A transcription of angle dependent potential functions into a spin operator notation is introduced. Potential functions and values for ε may be inferred from the data available in the literature for the interactions: $\text{H}_2\text{—He}$ ($\varepsilon \approx 1/4$) and $\text{H}_2\text{—H}_2$ ($\varepsilon \approx 1/20$). As far as elastic events are concerned, irreducible spin tensors of even rank only occur with the interaction potential and consequently with the scattering amplitude in order ε . The most important terms of the scattering amplitude of diatomic molecules are quadratic in the spins. These terms are discussed in detail. In order ε^2 the scattering amplitude also contains irreducible spin tensors of odd rank. A knowledge of the orders of magnitude of the various spin — dependent terms is of interest for the SENFTLEBEN-BEENAKKER effect and for NMR in polyatomic gases.

The binary scattering amplitude (operator) for rotating molecules can be divided into a part which commutes (spherical part) and one which does not commute (nonspherical part) with the sum of the rotational angular momenta (spins) of two colliding particles (diamagnetic molecules).

The spin dependence of the (nonspherical) scattering amplitude is of crucial importance for the kinetic theory of polyatomic gases as far as it is concerned with the influence of an external magnetic field on the classical transport properties¹ (SENFTLEBEN-BEENAKKER effect²).

Furthermore, the nonspherical part of the scattering amplitude determines the magnitude of the rotational relaxation constant which, in turn, is of interest for the interpretation of NMR data³ obtained for polyatomic gases. Sound absorption

measurements⁴ in polyatomic gases yield information on rotational transitions caused by inelastic collisions. The characteristic relaxation time is also determined by the nonsphericity of the scattering amplitude.

Theoretical investigations so far have mainly been concerned with effective cross sections for rotational transitions⁵ rather than with the calculation of the nonspherical scattering amplitude which contains more information and is needed for the SENFTLEBEN-BEENAKKER effect.

A “phenomenological” M -matrix theory which yields the most general form of a spin-dependent scattering amplitude subject to parity and time reversal invariance could be applied to molecular collisions much as it has been used for nuclear collisions⁶ and nuclear reactions⁷. It seems desirable,

¹ L. WALDMANN, in Proc. of the International Seminar on the Transport Properties of Gases, Brown University, Providence, R. J. 1964. — L. WALDMANN, in Fundamental Problems in Statistical Mechanics II, ed. E. G. D. COHEN, North Holland, Amsterdam 1968. — S. HESS and L. WALDMANN, Z. Naturforsch. **21 a**, 1529 [1966]. — F. R. MCCOURT and R. F. SNIDER, J. Chem. Phys. **46**, 2387 [1967]; **47**, 4117 [1967]. — Y. KAGAN and L. MAKSIMOV, Sov. Phys. JETP **24**, 1272 [1967].

² H. SENFTLEBEN, Phys. Z. **31**, 822, 961 [1930]. — H. ENGELHARDT and H. SACK, Phys. Z. **33**, 724 [1932]. — J. J. M. BEENAKKER, G. SCOLES, H. P. F. KNAAP, and R. M. JONKMAN, Phys. Letters **2**, 5 [1962]. — For a list of the literature on the Senftleben-Beenakker effect see BEENAKKER's review article in: Festkörperprobleme VIII, ed. O. MADELUNG, Vieweg, Braunschweig 1968.

³ A. ABRAGAM, The Principles of Nuclear Magnetism, Oxford University Press, Oxford 1961. — J. S. WAUGH, in Proc. of the XII Colloque Ampere, ed. R. BLINC, North Holland, Amsterdam 1967, p. 41. — E. TWARD and R. L. ARMSTRONG, J. Chem. Phys. **47**, 4068 [1967].

⁴ C. G. SLUIJTER, H. F. P. KNAAP, and J. J. M. BEENAKKER, Physica **30**, 745 [1964]; **31**, 915 [1965].

⁵ K. TAKAYANAGI, Suppl. Progr. Theor. Phys. **25**, 1 (1963).

⁶ L. WOLFENSTEIN, and J. ASHKIN, Phys. Rev. **85**, 947 [1952].

⁷ P. L. CSONKA, M. J. MORAVCSIK, and M. D. SCADRON, Ann. Phys. (N.Y.) **41**, 1 [1967]. — W. E. KÖHLER, and G. NACHTRAB, Diplomarbeiten, Erlangen 1966 (unpublished). W. E. KÖHLER and D. FICK, Z. Phys. **215**, 408 [1968].

⁸ The Cartesian components of \mathbf{s}_1 and \mathbf{s}_2 separately obey the angular momentum commutation relations; of course, \mathbf{s}_1 commutes with \mathbf{s}_2 .



however, to find out which of the various terms are the most important ones, the more so, as the number of possible terms increases rapidly with the magnitude of the spins involved.

Such an analysis shall be given here for elastic collisions (i.e., where the directions of the spins but not their magnitudes may be affected by collisions) of homonuclear diatomic molecules with small nonsphericity. In particular "diatomic molecule-spherical particle" and "diatomic molecule-diatom molecule" collisions shall be considered.

The starting point is the Lippmann-Schwinger equation which connects the scattering amplitude with the interaction potential. Although we are far from solving this integral equation analytically with a given nonspherical interaction potential in an approximation which is reasonable for molecular collisions, we are able to indicate the order of magnitude of the various spin-dependent terms of the scattering amplitude. This is already of great help for understanding some features of the SENFTLEBEN-BEENAKKER effect.

§ 1. Connection between Scattering Amplitude and Interaction Potential

We are concerned with the binary scattering amplitude operator a in the center of mass system and on the energy shell. For elastic collisions of particles with spin it depends on the relative kinetic energy $E = (1/2m)p^2$ (m : reduced mass), on the unit vectors \mathbf{e}' and \mathbf{e} specifying the directions of the initial and final relative momenta $\mathbf{p}' = p\mathbf{e}'$ and $\mathbf{p} = p\mathbf{e}$, respectively, and on the spin vector operators \mathbf{s}_1 and \mathbf{s}_2 (in units of \hbar) of the colliding particles (labelled by 1 and 2), i.e.

$$a = a(E, \mathbf{e}, \mathbf{e}'; \mathbf{s}_1, \mathbf{s}_2). \quad (1.1)$$

The scattering amplitude is related to the scattering \mathcal{T} -matrix on the energy shell by⁹

$$a(E, \mathbf{e}, \mathbf{e}'; \mathbf{s}_1, \mathbf{s}_2) = -\frac{m}{2\pi\hbar^2} \mathcal{T}(E, \mathbf{e}, \mathbf{e}'; \mathbf{s}_1, \mathbf{s}_2). \quad (1.2)$$

Here \mathcal{T} occurs in the momentum representation; it is linked with the \mathcal{T} -matrix in x -representation by

$$\begin{aligned} \mathcal{T}(E, \mathbf{e}, \mathbf{e}'; \mathbf{s}_1, \mathbf{s}_2) \\ = \frac{1}{\Omega} \iint e^{-ik\mathbf{e}\cdot\mathbf{x}} \mathcal{T}(\mathbf{x}, \mathbf{x}'; \mathbf{s}_1, \mathbf{s}_2) e^{ik\mathbf{e}'\cdot\mathbf{x}'} d^3x d^3x', \end{aligned} \quad (1.3)$$

⁹ e.g. M. L. GOLDBERGER, and K. M. WATSON, *Collision Theory*, Wiley, New York 1964, p. 236.

with $k = p/\hbar$; $\Omega = \int d^3x$ is a space volume (volume of quantization).

The scattering amplitude defined by (1.2) has the dimension of a length. The factor occurring there has been chosen such that

$$\begin{aligned} \bar{\sigma}(E, \mathbf{e}' \cdot \mathbf{e}) = \text{tr}_1 \text{tr}_2 \{ a^\dagger(E, \mathbf{e}, \mathbf{e}'; \mathbf{s}_1, \mathbf{s}_2) \\ \cdot a(E, \mathbf{e}, \mathbf{e}'; \mathbf{s}_1, \mathbf{s}_2) \} / (2S_1 + 1)(2S_2 + 1) \end{aligned} \quad (1.4)$$

is a spin-averaged differential cross section. Here tr_i denotes the trace with respect to the spin indices of particle i ; S_i is the magnitude of the relevant spin.

The \mathcal{T} -matrix, in turn, is connected with the interaction potential \mathcal{V} by the Lippmann-Schwinger equation. The formal solution of this equation reads (in a representation-invariant notation)

$$\mathcal{T} = \mathcal{V}(1 + \mathcal{G}\mathcal{V}). \quad (1.5)$$

Here \mathcal{G} is the appropriate Green's function for outgoing waves pertaining to the full Hamiltonian.

§ 2. Expansion of the \mathcal{T} -Matrix with Respect to the Nonspherical Potential

In space representation the interaction potential \mathcal{V} depends on the position vector \mathbf{x} pointing from the c.m. of molecule 1 to the c.m. of molecule 2, and on the spin vectors \mathbf{s}_1 and \mathbf{s}_2 . It can be divided into a spherical part V depending on the distance r (and possibly on the scalar $\mathbf{s}_1 \cdot \mathbf{s}_2$) and a nonspherical part εv

$$\mathcal{V} = V + \varepsilon v. \quad (2.1)$$

The nonspherical part may be written as

$$\varepsilon v(\mathbf{x}, \mathbf{s}_1, \mathbf{s}_2) = \varepsilon \sum_{n>0} v_n(r) U_n(\hat{\mathbf{x}}, \mathbf{s}_1, \mathbf{s}_2), \quad (2.2)$$

where U_n is a function of the unit vector $\hat{\mathbf{x}} = r^{-1}\mathbf{x}$ and the spin vectors but not of the distance r .

The numerical factor ε (nonsphericity parameter) is chosen in such a way that the leading $v_n(r)$ is of the same magnitude as $V(r)$. For the nonspherical potentials we found in the literature, ε is approximately in the range from 0.05 to 0.3. In these cases, it seems appropriate to expand \mathcal{T} with respect to ε , i.e., with respect to powers of the nonspherical part of the interaction potential:

$$\mathcal{T} = T^{(0)} + \varepsilon T^{(1)} + \varepsilon^2 T^{(2)} + \dots \quad (2.3)$$

Using (1.5) and

$$\mathcal{G} = G(1 + \varepsilon v\mathcal{G}), \quad (2.4)$$

where G is the Green's function pertaining to the kinetic energy plus the spherical interaction potential V , one readily finds

$$\begin{aligned} T^{(0)} &= V(1 + GV), \\ T^{(1)} &= (1 + VG)v(1 + GV), \\ T^{(2)} &= (1 + VG)vGv(1 + GV). \end{aligned} \quad (2.5)$$

Note that this perturbation expansion with respect to the nonspherical part of the interaction potential is quite different from a Born approximation (which cannot be used for molecular collisions at room temperature) since the dominant spherical part of the potential is here fully taken into account.

Next we consider several examples of nonspherical interaction potentials which have been proposed for diatomic molecule-spherical particle collisions.

§ 3. Spin-Dependent Potential for "Diatomic Molecule-Spherical Particle" Interaction

We first consider the collision of a rotating diatomic molecule with a spherical particle. Collisions of this type occur with mixtures of diatomic and monatomic gases as well as in H_2 gas where p- H_2 in the rotational ground state can be treated as spherically symmetric particle.

The interaction potential will depend on the distance r between the particles and on the angle χ between the axis of the molecule and the vector connecting its center of mass to the spherical particle. The dependence on the angle χ can be expressed in terms of Legendre polynomials $P_n(\cos \chi)$:

$$\mathcal{V}(r, \chi) = V(r) + \sum_{n \geq 1} V_n(r) P_n(\cos \chi). \quad (3.1)$$

Here $V(r)$ is the spherical part of the potential. If we confine our attention to homonuclear diatomic molecules such as H_2 and N_2 , then only even Legendre polynomials occur in the sum in (3.1).

The short range part of the angle-dependent interaction potential is linked with the deviation of the shape of the molecule from spherical symmetry⁵. The long range part of the nonspherical interaction potential (for particles without a permanent electric dipole moment) is related to the static quadrupole-quadrupole interaction and even more to induced multipole-multipole interactions. In both cases the P_2 -term will be the most important one and all higher Legendre polynomials may be neglected⁵.

In order to find the connection between the nonspherical potential (3.1) and a spin-dependent poten-

tial as used in (2.2), (2.4), (2.5) we first observe that one has

$$P_2(\cos \chi) = \frac{3}{2} \overline{u_\mu u_\nu} \hat{x}_\mu \hat{x}_\nu, \quad (3.2)$$

where \mathbf{u} is a unit vector parallel to the molecular axis. Cartesian components of vectors and tensors are denoted by Greek indices. For these the summation convention is used. The bar $\overline{}$ denotes the irreducible (symmetric traceless) part of a tensor, e.g.

$$\overline{a_\mu b_\nu} = \frac{1}{2} (a_\mu b_\nu + a_\nu b_\mu) - \frac{1}{3} \mathbf{a} \cdot \mathbf{b} \delta_{\mu\nu}, \quad (3.3)$$

where \mathbf{a} and \mathbf{b} are vectors and $\delta_{\mu\nu}$ is the isotropic unit tensor of rank 2.

Next we have to express the tensor $\overline{u_\mu u_\nu}$ as a "spin-operator", i.e. given the spin vector operator \mathbf{s} (with $\mathbf{s} \cdot \mathbf{u} = 0$; rotator!) classically speaking, an average over the orientation of \mathbf{u} in a plane perpendicular to \mathbf{s} has to be taken. The magnitude S of the spin is taken to be constant (elastic scattering!). In operator notation (with respect to the magnetic quantum numbers) we have with a proportionality constant c

$$(\overline{u_\mu u_\nu})_{\text{op}} = c \overline{s_\mu s_\nu}, \quad (3.4)$$

since $\overline{s_\mu s_\nu}$ is the only irreducible spin tensor of rank 2 which is available. The subscript "op" refers to the operator notation (with respect to spin indices). The constant c may be found by multiplying (3.4) with $s_\mu s_\nu$ (and contracting) and using $\mathbf{s} \cdot \mathbf{u} = 0$, and

$$s_\mu s_\nu \overline{s_\mu s_\nu} = \frac{2}{3} S(S+1) [S(S+1) - \frac{3}{4}].$$

Here S is the magnitude of the spin, i.e. $\mathbf{s} \cdot \mathbf{s} = S(S+1)$. Note that the bracket vanishes for $S = \frac{1}{2}$.

Thus, according to (3.2), one finally obtains

$$(P_2(\cos \chi))_{\text{op}} = -\frac{3}{4} [S(S+1) - \frac{3}{4}]^{-1} \overline{s_\mu s_\nu} \hat{x}_\mu \hat{x}_\nu. \quad (3.5)$$

This result is a special case of the more general formulas for the "transcription" of $P_l(\cos \chi)$ into a "spin-operator" notation which, also for inelastic collisions, may be obtained by using rigid rotator wave functions and Clebsch-Gordan algebra. For details, see the appendix.

Thus, we have to deal with an interaction potential of the type

$$\mathcal{V} = V(r) + \varepsilon v(r) [S(S+1) - \frac{3}{4}]^{-1} \hat{x}_\mu \hat{x}_\nu \overline{s_\mu s_\nu}. \quad (3.6)$$

The nonsphericity parameter ε is independent of S if the distance of the two atoms of the diatomic

molecule does not depend on S (rigid rotator). Here and in the following, we write $v(r)$ instead of $v_2(r)$ (cf. 2.2).

Next we want to give some examples for functions $V(r)$, $v(r)$ and the nonsphericity parameter ε as they can be obtained from data available in the literature by using relation (3.5). Our aim is to show clearly the meaning of ε for various potentials and to give numerical values for it. Therefore, we only state the functional dependence of V and v on r but not the numerical values of the constants involved. Here we consider the interaction of rotating H_2 molecules with p- H_2 in the rotational ground state and with He atoms.

1. (rotating) H_2 -p- H_2 (rotational ground state)

a) In connection with an attempt to explain the measured viscosity¹⁰ of H_2 at low temperatures NIBLETT and TAKAYANAGI¹¹ used the following functions for the interaction of o- H_2 with ground-state p- H_2 :

$$\begin{aligned} V(r) &= A(1 + ar)e^{-\alpha r} - Br^{-6} - Cr^{-8}, \\ v(r) &= 1.07A(1 - a'r)e^{-\alpha r} + Br^{-6}, \end{aligned} \quad (3.7)$$

$$\text{and} \quad \varepsilon = 0.050. \quad (3.8)$$

There occur quite a lot of (positive) constants A , B , C , a , a' , α which may be inferred from Ref.¹¹. Remarkable is the rather small value for ε .

b) In dealing with rotational transitions (where the magnitudes of the spins are changed during a collision) TAKAYANAGI¹² used a Morse potential for both p- H_2 and o- H_2 interactions with ground state p- H_2 :

$$\begin{aligned} V(r) &= D(e^{-\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)/2}), \\ v(r) &= -De^{-\alpha(r-r_0)}, \end{aligned} \quad (3.9)$$

$$\text{with} \quad \varepsilon = 0.056. \quad (3.10)$$

Here D , α and r_0 are constants.

2. (rotating) H_2 -He

a) The following potential functions for the o- H_2 -He interaction have been used by Waugh and co-workers (see Ref.³) in order to calculate rotational relaxation constants which can be compared with

NMR data:

$$\begin{aligned} V(r) &= A(e^{-\alpha r} - br^{-6}), \\ v(r) &= -A(e^{-\alpha r} - b'r^{-6}) \end{aligned} \quad (3.11)$$

$$\text{with} \quad \varepsilon = 0.142. \quad (3.12)$$

Again A , α , b and $b' \approx 0.4b$ are constants.

Here the nonsphericity parameter ε is almost three times larger than in the case of the H_2 - H_2 interaction. This might be connected with the fact that the He-atom is smaller than the H_2 molecule.

b) ROBERTS¹³ calculated the (angle dependent) interaction energy of a H_2 molecule with a He atom from first principles using a simple wave function made up of 1S orbitals centered on the three nuclei. It turned out that he could represent the numerically computed interaction energy quite accurately by a potential function of the type (3.1) with only a spherical term and a $P_2(\cos \chi)$ -term. His results can be expressed in the following form of the repulsive part of the interaction:

$$\begin{aligned} V(r) &= Ce^{-\alpha r}, \\ v(r) &= -Ce^{-\alpha r}, \end{aligned} \quad (3.13)$$

$$\text{with} \quad \varepsilon = 0.282, \quad (3.14)$$

C and α again being constants.

Note that ROBERTS' nonsphericity parameter (3.14) is twice as large as the value (3.12) given by WAUGH.

The values for ε quoted here apply to the lowest rotational states of the H_2 molecules (i.e. for rotational quantum numbers 1, 2, possibly for 3 and 4 too). TAKAYANAGI^{5,12} used the same nonsphericity for any rotational state of the H_2 molecule. ROBERTS¹³, however, showed that the nonsphericity is quite sensitive to the distance between the protons (bond length) in the H_2 molecule. Hence the nonsphericity may be expected to increase with the rotational quantum number.

§ 4. Scattering Amplitude for "Diatomic-Monatomic" Collisions

With the nonspherical interaction potential (3.6) the term of the \mathcal{T} -matrix which is linear in the nonsphericity parameter ε obviously will contain the

¹⁰ E. W. BECKER, and O. STEHL, Z. Phys. **133**, 615 [1952].

¹¹ P. D. NIBLETT, and K. TAKAYANAGI, Proc. Roy. Soc. London A **250**, 222 [1959].

¹² K. TAKAYANAGI, Proc. Phys. Soc. London A **70**, 348 [1957]. — Sci. Rep. Saitama Univ. A **3**, 87 [1959].

¹³ C. S. ROBERTS, Phys. Rev. **131**, 203, 209 [1963].

second rank irreducible spin tensor. This term (cf. 2.5) can be written as

$$T^{(1)} = T_{\mu\nu}^{(1)} [S(S+1) - \frac{3}{4}]^{-1} \overline{s_\mu s_\nu}. \quad (4.1)$$

According to (2.5) the tensor $T_{\mu\nu}^{(1)}$ is given by

$$T_{\mu\nu}^{(1)} = (1 + VG) \overline{\hat{x}_\mu \hat{x}_\nu} v(r) (1 + GV). \quad (4.2)$$

An operator notation has been used here. Note that the Green's function G is neither diagonal in x - nor in p -representation.

In view of (4.1) the part of the scattering amplitude which is linear in ε will also contain $\overline{s_\mu s_\nu}$. Hence up to terms of order ε the scattering amplitude reads

$$a = a_0 + \varepsilon A_{\mu\nu} [S(S+1) - \frac{3}{4}]^{-1} \overline{s_\mu s_\nu} + O(\varepsilon^2). \quad (4.3)$$

Here a_0 is the spherical part of the scattering amplitude which is connected to $T^{(0)}$ (cf. 2.5) according to (1.2) and (1.3). The tensor $A_{\mu\nu}$ is related to (4.2) by

$$A_{\mu\nu} = -\frac{m}{2\pi\hbar^2} T_{\mu\nu}^{(1)}(E, \mathbf{e}, \mathbf{e}'), \quad (4.4)$$

where $T_{\mu\nu}^{(1)}$ occurs in momentum representation (cf. 1.3). On the other hand, $A_{\mu\nu}$ also can be expressed in terms of irreducible tensors which can be constructed from the Cartesian components of the unit vectors \mathbf{e} and \mathbf{e}' :

$$A_{\mu\nu} = 2a_1 \overline{e_\mu e'_\nu} + a_2 (\overline{e_\mu e_\nu} + \overline{e'_\mu e'_\nu}). \quad (4.5)$$

Here a_1 and a_2 are scalar functions (like a_0) depending on the relative kinetic energy E and the angle of deflection ϑ defined by

$$\mathbf{e} \cdot \mathbf{e}' = \cos \vartheta. \quad (4.6)$$

These functions are linked with (4.5) by

$$\begin{aligned} a_1 &= (c_2 A_1 - c_{12} A_2)/D, \\ a_2 &= (c_1 A_2 - c_{12} A_1)/D \end{aligned} \quad (4.7)$$

where the abbreviations

$$A_1 = 2e_\mu e'_\nu A_{\mu\nu}, \quad A_2 = (e_\mu e_\nu + e'_\mu e'_\nu) A_{\mu\nu}, \quad (4.8)$$

$$\begin{aligned} c_1 &= 2 + \frac{2}{3} \cos^2 \vartheta, \quad c_{12} = \frac{8}{3} \cos \vartheta, \\ c_2 &= \frac{2}{3} + 2 \cos^2 \vartheta, \end{aligned} \quad (4.9)$$

and $D = c_1 c_2 - c_{12}^2$ have been used.

Next we consider the terms of the \mathcal{T} -matrix which are quadratic in ε . In particular we want to show that the interaction potential (3.6) implies that the scattering amplitude contains a " $\mathbf{n} \cdot \mathbf{s}$ -term" of

order ε^2 :

$$\varepsilon^2 a_3 [S(S+1) - \frac{3}{4}]^{-1} \mathbf{n} \cdot \mathbf{s}, \quad (4.10)$$

where

$$\mathbf{n} = \mathbf{e}' \times \mathbf{e} / \sin \vartheta \quad (4.11)$$

is a unit vector perpendicular to the collision plane and $a_3 = a_3(E, \vartheta)$ is a scalar. To this end we note that

$$T^{(2)} = T_{\mu\nu, \mu'\nu'}^{(2)} [S(S+1) - \frac{3}{4}]^{-2} \overline{s_\mu s_\nu s_{\mu'} s_{\nu'}} \quad (4.12)$$

contains a product of two second rank irreducible spin tensors which can be expressed by a linear combination of irreducible spin tensors of rank 0 to 4, i.e., one has

$$\begin{aligned} T^{(2)} &= c_0 T_{\mu\nu, \mu\nu}^{(2)} + c_1 s_\lambda \varepsilon_{\lambda\mu\nu} T_{\mu\nu, \nu\lambda}^{(2)} \cdots \\ &+ c_4 \overline{s_\mu s_\nu s_{\mu'} s_{\nu'}} T_{\mu\nu, \mu'\nu'}^{(2)} \end{aligned} \quad (4.13)$$

with the constants c_i ($i = 0, 1, \dots, 4$). These constants may be determined by multiplying (4.13) with 1, s_κ, \dots and taking the trace on both sides. Thus one obtains (for spin traces see e.g. HESS and WALDMANN, Ref.¹)

$$\begin{aligned} c_0 &= \frac{2}{15} S(S+1) [S(S+1) - \frac{3}{4}], \\ c_1 &= i \frac{2}{5} [S(S+1) - \frac{3}{4}]. \end{aligned} \quad (4.14)$$

The 4th rank tensor $T_{\mu\nu, \mu'\nu'}^{(2)}$, in analogy to (4.2), is given by

$$T_{\mu\nu, \mu'\nu'}^{(2)} = (1 + VG) \overline{\hat{x}_\mu \hat{x}_\nu} v(r) G \overline{\hat{x}_{\mu'} \hat{x}_{\nu'}} v(r) (1 + GV). \quad (4.15)$$

Obviously, the first term in (4.13) is a spherical one. As, however, it only contributes in order ε^2 , it is negligible compared with $T^{(0)}$. The terms in (4.13) containing the irreducible spin tensors of rank 2, 3, 4 (in a linear way) are disregarded here, for there is already a term of order ε containing a spin tensor of rank 2; those of rank 3 and 4 are not of interest for the SENFTLEBEN-BEENAKKER effect for linear molecules. Fourth rank spin tensors, however, are of importance for regular octahedral molecules^{13a}.

The second term in (4.13) yields the desired $\mathbf{n} \cdot \mathbf{s}$ -term (4.10) of the scattering amplitude if one takes (4.13) in p -representation [cf. (1.2)]. Since $T_{\mu\nu, \mu'\nu'}^{(2)}$ has positive parity the vector $\varepsilon_{\lambda\mu\nu} T_{\mu\nu, \nu\lambda}^{(2)}$ is an axial vector. The only axial vector which can be constructed from $\mathbf{p} = p\mathbf{e}$ and $\mathbf{p}' = p'\mathbf{e}'$ is proportional to the unit vector \mathbf{n} , thus one has

$$\varepsilon_{\lambda\mu\nu} T_{\mu\nu, \nu\lambda}^{(2)}(E, \mathbf{e}, \mathbf{e}') = C n_\lambda. \quad (4.16)$$

^{13a} S. HESS, Phys. Letters **28 A**, 87 [1968].

The scalar function C is easily obtained by multiplying (4.16) with n_λ . Hence the scalar function a_3 is given by (cf. 1.2 and 4.14)

$$a_3 = -\frac{m}{2\pi\hbar^2} i \frac{2}{5} n_\lambda \varepsilon_{\lambda\mu\nu} T_{\mu e, r e}^{(2)}(E, \mathbf{e}, \mathbf{e}'). \quad (4.17)$$

§ 5. Spin-Dependent Potential for the Interaction of Two Diatomic Molecules

Now we consider the interaction of two diatomic molecules. The interaction potential corresponding to (3.1) in general will depend on three angles χ_1 , χ_2 and φ . Here χ_i ($i = 1, 2$) is the angle between the molecular axis of molecule i and \mathbf{x} (\mathbf{x} : position vector of the c.m. of the first molecule relative to the c.m. of the second molecule), $\varphi = \varphi_1 - \varphi_2$ is the angle between the projections of the molecular axes on a plane perpendicular to \mathbf{x} . Thus the most general interaction potential will be of the form

$$\mathcal{V}(r, \chi_1, \chi_2, \varphi) \quad (5.1)$$

$$= \sum_{l'l'} \sum_m V_{ll', m}(r) [Y_{lm}^*(\chi_1, \varphi_1) Y_{l'm}(\chi_2, \varphi_2) + \text{c.c.}].$$

The $Y_{lm}(\chi_i, \varphi_i)$ are the usual spherical harmonics (e.g. see Ref. ⁹). The summation over m ranges from $m = 0$ to $m = \min(l, l')$, the l and l' summations run from 0 to ∞ .

If the $V_{ll', m}$ with $m \neq 0$ can be neglected compared with $V_{ll', 0}$ — this indeed is fulfilled for the $\text{H}_2\text{-H}_2$ interaction — one may write (5.1) in terms of Legendre polynomials using

$$Y_{l0}(\chi) = Y_{l0}^*(\chi) = \sqrt{(2l+1)/4\pi} P_l(\cos \chi).$$

Thus one obtains

$$V(r, \chi_1, \chi_2) = \sum_{l'l'} V_{ll'}(r) P_l(\cos \chi_1) P_{l'}(\cos \chi_2), \quad (5.2)$$

with

$$V_{ll'}(r) = \frac{1}{2\pi} \sqrt{2l+1} \sqrt{2l'+1} V_{ll', 0}(r). \quad (5.3)$$

In order to get rid of the angle φ one might also average (5.1) over this angle. Now one also finds an interaction potential like (5.2), but then the relation (5.3) is no longer fulfilled.

For identical molecules one has $V_{ll'} = V_{l'l}$. If the molecules are homonuclear both l and l' are even.

For identical homonuclear diatomic molecules the most important nonspherical terms will be proportional to

$$P_2(\cos \chi_1) + P_2(\cos \chi_2)$$

and

$$P_2(\cos \chi_1) P_2(\cos \chi_2). \quad (5.4)$$

Hence we will have to deal with a spin-dependent interaction potential analogous to (3.6)

$$\mathcal{V} = V(r) + \varepsilon v_{20}(r) [S_1^{-2}(1) \overline{s_{1\mu} s_{1\nu}} + S_1^{-2}(2) \overline{s_{2\mu} s_{2\nu}}] \hat{x}_\mu \hat{x}_\nu$$

$$+ \varepsilon v_{22}(r) S_1^{-2}(1) S_1^{-2}(2) \overline{s_{1\mu} s_{1\nu} s_{2\mu'} s_{2\nu'}} \hat{x}_\mu \hat{x}_\nu \hat{x}_{\mu'} \hat{x}_{\nu'}. \quad (5.5)$$

Relation (3.5) has been used in arriving at (5.5). The rotational spin vectors of the interacting molecules are denoted by \mathbf{s}_1 and \mathbf{s}_2 . The abbreviation

$$S_i^2(i) = S_i(S_i + 1) - \frac{3}{4}, \quad (5.6)$$

— where S_i is the magnitude of the spin of particle i — has been introduced for convenience.

Again $V(r)$ is the spherical part of the interaction potential.

Next we mention briefly two examples for the potential functions $V(r)$, $v_{20}(r)$, $v_{22}(r)$ and the value of the nonsphericity parameter ε . Both examples refer to the $\text{H}_2\text{-H}_2$ interaction.

a) In Ref. ¹¹ NIBLETT and TAKAYANAGI gave a rather complicated angle dependent interaction potential for the $\text{H}_2\text{-H}_2$ interaction. But the leading nonspherical terms are of the type (5.4). From the data they gave one may infer V , v_{20} and v_{22} . Both V and v_{20} contain short range terms similar to (3.7) and long range terms proportional to r^{-6} and r^{-5} , v_{22} only contains terms proportional to r^{-6} and r^{-5} . The nonsphericity parameter is of the order 0.05.

b) Dealing with rotational transitions of H_2 molecules, TAKAYANAGI^{5,12} used a Morse potential with V and $v_{20}(r) = v(r)$ as given by (3.9), $v_{22}(r) = 0$, and $\varepsilon = 0.056$.

For further details on intermolecular forces reference is made to the reviews articles in vol. 12 of „Advances in Chemical Physics“ ^{14a}

§ 6. Scattering Amplitude for the Collision of Two Diatomic Molecules

The spin dependent interaction potential (5.5) implies that the scattering amplitude for the collisions of two diatomic molecules with rotational spin vectors \mathbf{s}_1 and \mathbf{s}_2 reads up to terms of order ε :

$$a = a_0 + \varepsilon A_{\mu\nu} [S_1^{-2}(1) \overline{s_{1\mu} s_{1\nu}} + S_1^{-2}(2) \overline{s_{2\mu} s_{2\nu}}]$$

$$+ \varepsilon B_{\mu\nu, \mu'\nu'} S_1^{-2}(1) S_1^{-2}(2) \overline{s_{1\mu} s_{1\nu} s_{2\mu'} s_{2\nu'}} + O(\varepsilon^2). \quad (6.1)$$

^{14a} J. O. HIRSCHFELDER (ed.), Intermolecular Forces, Interscience, New York 1967.

Here a_0 is again the spherical part of the scattering amplitude. The tensor $A_{\mu\nu}$ already occurred with (4.3); it is related to $v_{20}(r)$ by (4.4) and (4.2) where $v(r)$ should be replaced by $v_{20}(r)$. The 4th rank tensor $B_{\mu\nu, \mu'\nu'}$ is defined analogously to $A_{\mu\nu}$; i.e. in analogy with $T_{\mu\nu}^{(1)}$, a tensor $T_{\mu\nu, \mu'\nu'}^{(1)}$ may be introduced by (cf. 4.1)

$$T_{\mu\nu, \mu'\nu'}^{(1)} = (1 + VG) \overline{\hat{x}_\mu \hat{x}_\nu} \overline{\hat{x}_{\mu'} \hat{x}_{\nu'}} v_{22}(r) (1 + GV). \quad (6.2)$$

Then, in analogy with (4.4), one has

$$B_{\mu\nu, \mu'\nu'} = -\frac{m}{2\pi\hbar^2} T_{\mu\nu, \mu'\nu'}^{(1)}(E, \mathbf{e}, \mathbf{e}'). \quad (6.3)$$

The second rank tensor $A_{\mu\nu}$ has been expressed, through Eq.(4.5), in terms of irreducible tensors which can be constructed from the Cartesian components of the unit vectors \mathbf{e} and \mathbf{e}' . An expression like (4.5) for $B_{\mu\nu, \mu'\nu'}$ is not given here, since the term containing the product of the second rank spin tensors of particles 1 and 2 has little importance for the SENTLEBEN-BEENAKKER effect. Such a term, however, will contribute to the relaxation constants for the vector and tensor polarizations.

Finally we note that the scattering amplitude again contains a „ $\mathbf{n} \cdot \mathbf{s}$ -term” of order ε^2

$$\varepsilon^2 a_3 [S_1^{-2}(1) \mathbf{s}_1 + S_1^{-2}(2) \mathbf{s}_2] \cdot \mathbf{n}. \quad (6.4)$$

The scalar a_3 may be inferred from (4.17) and (4.15) where $v(r)$ has to be replaced by $v_{20}(r)$.

§ 7. Concluding Remarks

i) The leading nonspherical term of the interaction potential of two rotating homonuclear molecules (with equal magnitude S of the spin for simplicity here) is proportional to (cf. 5.5)

$$(\overline{s_{1\mu} s_{1\nu}} + \overline{s_{2\mu} s_{2\nu}}) \hat{x}_\mu \hat{x}_\nu. \quad (7.1)$$

Thus the scattering amplitude contains a term of order ε proportional to (cf. 6.1)

$$(\overline{s_{1\mu} s_{1\nu}} + \overline{s_{2\mu} s_{2\nu}}) A_{\mu\nu}, \quad (7.2)$$

and the term proportional to

$$(\mathbf{s}_1 + \mathbf{s}_2) \cdot \mathbf{n} \quad (7.3)$$

is of order ε^2 (cf. 6.4). For the specific examples which were considered, the nonsphericity parameter

ranged from 0.05 to 0.3. Hence the term (7.3) is small compared with (7.2).

This explains why “odd terms in rotational angular momentum”¹⁴ play a minor role with the SENTLEBEN-BEENAKKER effect of linear nonpolar molecules. It is the term (7.3) of the scattering amplitude, namely, which determines the influence of moments linear in the spin vector (“odd terms”) on the heat conductivity and viscosity¹⁵. The influence of moments containing the second rank irreducible spin tensor (“even terms”) on the classical transport properties, however, is determined by the term (7.2) of the scattering amplitude¹⁵. Hence one may expect that the dependence of the classical transport properties on the magnitude of the magnetic field divided by the density (or pressure) of the gas will be governed by even spin terms of the distribution function. This indeed is observed experimentally² (even for the cases where inelastic collisions are important).

For a nonsphericity parameter ε of order 1, however, the perturbation expansion (2.3) may no longer be used. The terms (7.2) and (7.3) of the scattering amplitude then may be expected to be of equal order of magnitude.

ii) The scattering amplitude (4.3, 10; 6.1, 4) contains several scalar functions a_i ($i = 0, 1, 2, 3$) depending on the relative kinetic energy and the angle of deflection in the center of mass system. It would be highly desirable to evaluate these functions to a reasonable accuracy with a suitably chosen spherical interaction V and a realistic $v(r)$ or $v_{20}(r)$.

iii) So far, have been concerned only with energetically elastic scattering events. A similar analysis for inelastic collisions (where the magnitude of the rotational spin is changed) shall be given in a subsequent publication.

We gratefully acknowledge fruitful discussions with Prof. Dr. L. WALDMANN.

Appendix:

Transcription of Legendre Polynomials P_l into a Spin Operator Notation

The potential function for the interaction of a diatomic molecule with a monatomic particle contains the Legendre polynomials $P_l(\cos \chi)$ (cf. 3.1).

¹⁴ A. C. LEVI, and F. R. MCCOURT, *Physica* **38**, 415 [1968].

¹⁵ S. HESS, and L. WALDMANN, *Z. Naturforsch.* **23a**, 1893 [1968].

Here χ is the angle between the unit vectors \mathbf{u} and \mathbf{x} which characterize the directions of the molecular axis and of the position vector $\mathbf{x} = r\hat{\mathbf{x}}$ from the center of mass of the molecule to the monatomic particle, i.e.,

$$\mathbf{u} \cdot \hat{\mathbf{x}} = \cos \chi. \quad (\text{A.1})$$

In order to obtain the spin dependent interaction potential pertaining to this potential function, one needs a transcription of the P_l ($l = 1, 2, \dots$) into a spin operator notation. This transcription shall now be given including the case where transitions between the rotational energy levels of the molecule occur.

The diatomic molecule is treated as a rigid rotator. Then the rotational wave functions $|SM\rangle$ are spherical harmonics Y_{SM}

$$|SM\rangle = Y_{SM}(\vartheta, \varphi) \equiv Y_{SM}(\mathbf{u}). \quad (\text{A.2})$$

Here ϑ and φ are the polar angles of the unit vector \mathbf{u} with respect to the (arbitrary) direction of quantization which is characterized by the unit vector \mathbf{a} ($\varphi = 0$ if \mathbf{u} lies in the plane determined by $\hat{\mathbf{x}}$ and \mathbf{a}). Clearly S is the magnitude of the spin and M is a magnetic quantum number:

$$\begin{aligned} \mathbf{s} \cdot \mathbf{s} |SM\rangle &= S(S+1) |SM\rangle, \\ \mathbf{a} \cdot \mathbf{s} |SM\rangle &= M |SM\rangle. \end{aligned} \quad (\text{A.3})$$

Matrix elements of $P_l(\cos \chi)$ with respect to the wave functions $|SM\rangle$ have to be evaluated according to

$$\langle S'M' | P_l | SM \rangle = \int Y_{S'M'}^*(\mathbf{u}) P_l(\mathbf{u} \cdot \hat{\mathbf{x}}) Y_{SM}(\mathbf{u}) d^2u, \quad (\text{A.4})$$

with $d^2u = \sin \vartheta d\vartheta d\varphi$.

In order to perform this integration, we decompose $P_l(\mathbf{u} \cdot \hat{\mathbf{x}})$:

$$P_l(\mathbf{u} \cdot \hat{\mathbf{x}}) = \frac{4\pi}{2l+1} \sum_m Y_{lm}^*(\mathbf{u}) Y_{lm}(\hat{\mathbf{x}}), \quad (\text{A.5})$$

where $Y_{lm}(\hat{\mathbf{x}}) = Y_{lm}(\Theta, 0)$ with $\cos \Theta = \mathbf{a} \cdot \mathbf{x}$.

Then we note that the remaining integral can be expressed in terms of Clebsch-Gordan coefficients¹⁷:

$$\begin{aligned} \int Y_{S'M'}^*(\mathbf{u}) Y_{lm}^*(\mathbf{u}) Y_{SM}(\mathbf{u}) d^2u \\ = \sqrt{\frac{2S'+1}{4\pi}} (S'0, l0 | S0) (-1)^{S'-M'} \\ \cdot (SM, S' - M' | lm). \end{aligned} \quad (\text{A.6})$$

Now we observe that $(-1)^{S'-M'} (SM, S' - M' | lm)$ is a matrix element of the tensor operator^{7,16,17} in spin space which transforms like an adjoint spherical harmonic under a rotation of the coordinate system

$$\langle S'M' | T_{lm}^{S'S} | SM \rangle = (-1)^{S'-M'} (SM, S' - M' | lm). \quad (\text{A.7})$$

Thus we obtain

$$\begin{aligned} \langle S'M' | P_l | SM \rangle \\ = \sqrt{4\pi} \sqrt{\frac{2S'+1}{2l+1}} (S'0, l0 | S0) \sum_m Y_{lm}(\hat{\mathbf{x}}) \\ \cdot \langle S'M' | T_{lm}^{S'S} | SM \rangle. \end{aligned} \quad (\text{A.8})$$

Note that $(S'0, l0 | S0)$ vanishes unless $S' - S + l$ is even. In (A.8) the angle between $\hat{\mathbf{x}}$ and \mathbf{a} still occurs. The sum over m is a scalar product (of two spherical tensor operators). It reduces to one term with $m = 0$ if \mathbf{a} is parallel to $\hat{\mathbf{x}}$.

From the matrix element equation (A.8) one infers the following equation for „spin operators”

$$P_l^{S'S} = \sqrt{4\pi} \sqrt{\frac{2S'+1}{2l+1}} (S'0, l0 | S0) \sum_m Y_{lm}(\hat{\mathbf{x}}) T_{lm}^{S'S}. \quad (\text{A.9})$$

This relation holds for both elastic ($S = S'$) and inelastic ($S \neq S'$) processes.

Some useful relations for the $T_{lm}^{S'S}$ are

$$\begin{aligned} T_{lm}^{S'S} &= \sum_{M,M'} (-1)^{S'-M'} (SM, S' - M' | lm) \\ &\cdot |S'M'\rangle \langle SM|, \end{aligned} \quad (\text{A.10})$$

$$(T_{lm}^{S'S})^\dagger = (-1)^{S'-S+m} T_{l-m}^{SS'}, \quad (\text{A.11})$$

$$\text{tr} \{ T_{lm}^{S'S} (T_{l'm'}^{S'S})^\dagger \} = \delta_{ll'} \delta_{mm'}. \quad (\text{A.12})$$

Note that $T_{lm}^{S'S}$, and consequently $P_l^{S'S}$, vanishes unless $|S - S'| \leq l \leq S + S'$.

For $S = S'$ (elastic scattering) the scalar product occurring in (A.9) can be written as a scalar product of an irreducible Cartesian spin tensor with the tensor (of the same rank) constructed from the Cartesian components of $\hat{\mathbf{x}}$

$$\begin{aligned} \sqrt{4\pi} \sqrt{2S+1} \sum_m T_{lm}^{SS} Y_{lm}(\hat{\mathbf{x}}) \\ = \frac{(2l+1)!!}{l! S_0 S_1 \dots S_{l-1}} \overline{s_{\mu_1} \dots s_{\mu_l}} \hat{x}_{\mu_1} \dots \hat{x}_{\mu_l}. \end{aligned} \quad (\text{A.13})$$

¹⁶ S. DEVONS, and L. J. B. GOLDFARB, in Handbuch der Physik, ed. S. FLÜGGE, Vol. 42, 362, Springer, Berlin 1957.

¹⁷ A. R. EDMONDS, Angular Momentum in Quantum Mechanics, Princeton Univ. Press, Princeton, N.J. 1957.

The bar $\overline{}$ denotes the irreducible part of a tensor. The abbreviation

$$S_n = \left[S(S+1) - \frac{n}{2} \left(\frac{n}{2} + 1 \right) \right]^{1/2} \quad (\text{A.14})$$

has been used. Thus one obtains

$$P_l^{SS} = (S0, l0 | S0) \frac{(2l-1)!!}{l!} \frac{1}{S_0 S_1 \dots S_{l-1}} \quad (\text{A.15})$$

$$\cdot \overline{s_{\mu_1} \dots s_{\mu_l} \hat{x}_{\mu_1} \dots \hat{x}_{\mu_l}}.$$

For $l=2$, using $(S0, 20 | S0) = -S_0/2S_1$, one recovers (3.5),

$$P_2^{SS} = -\frac{3}{4S_1^2} \overline{s_{\mu} s_{\nu} \hat{x}_{\mu} \hat{x}_{\nu}}. \quad (\text{A.16})$$

Likewise, with $(S0, 40 | S0) = 3S_0 S_2 / 8S_1 S_3$, one finds for $l=4$

$$P_4^{SS} = \frac{105}{64} \frac{1}{S_1^2 S_3^2} \overline{s_{\mu_1} \dots s_{\mu_4} \hat{x}_{\mu_1} \dots \hat{x}_{\mu_4}}. \quad (\text{A.17})$$

Influence of a Magnetic Field on the Brownian Motion of Particles with Magnetic Moment

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The influence of a magnetic field on the diffusion of Brownian particles with a magnetic moment parallel to their internal angular momentum is discussed. Starting point is a generalized Fokker-Planck equation. Application of the moment method leads to a set of transport-relaxation equations. From them the diffusion tensor depending on the external field is inferred.

In a previous paper¹ the Brownian motion of (spherical) rotating particles has been studied on the basis of a generalized Fokker-Planck equation. Due to the coupling of the translational and rotational motions, a diffusion flow gives rise to a correlation between linear and angular velocities. This correlation, in turn, influences the value of the diffusion coefficient.

In this paper, it is assumed that the (neutral) Brownian particles have a magnetic moment parallel to their internal angular momentum. Then, in the presence of an external magnetic field $\mathbf{H} = H \mathbf{h}$ (where \mathbf{h} is a unit vector) the Brownian particles undergo a precessional motion with frequency ω_H which is equal to the gyromagnetic ratio times the magnitude H of the field. By this precessional motion the correlation between linear and angular velocities, existing in the transport situation without field, is partially destroyed. Consequently, the diffusion coefficient becomes a field-dependent second rank tensor. It is characterized by three scalar coefficients depending on the magnitude of the field. The magnetic field dependence of the diffusion is similar

to the influence of the magnetic field on the transport properties of dilute polyatomic gases (SENFTLEBEN-BEENAKKER effect²).

Firstly, we shall state the generalized Fokker-Planck equation in which the precessional motion of the internal angular momentum is taken into account. Then the transport-relaxation equations needed for the discussion of the diffusion problem in the presence of a magnetic field are given. Finally the diffusion tensor is inferred from these equations.

Generalized Fokker-Planck Equation

An ensemble of Brownian particles is described by the distribution function

$$F = F(t, \mathbf{x}, \mathbf{V}, \mathbf{W}). \quad (1)$$

Here t is the time, \mathbf{x} the position vector, and \mathbf{V} is the velocity of a particle (in units of a thermal velocity v_0). The difference between the actual internal angular velocity and the angular velocity due to a thermal equilibrium polarization in a magnetic field (both in units of a thermal angular velocity) is de-

¹ S. HESS, Z. Naturforsch. **23 a**, 597 [1968].

² H. SENFTLEBEN, Phys. Z. **31**, 822, 961 [1930]. — J. J. M. BEENAKKER et al., Phys. Letters **2**, 5 [1962]. For a list of

the literature on the SENFTLEBEN-BEENAKKER effect see BEENAKKER's review article in: Festkörperprobleme VIII, ed. O. MADELUNG, Vieweg, Braunschweig 1968.