Formal and Approximate Evaluations of a Number of Collision Integrals for Diatomic Molecules

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Dedicated to Prof. Dr. L. Waldmann on the occasion of his 60th birthday

Expressions which are exact in the distorted wave Born approximation are derived for a number of kinetic theory collision cross sections, viz., $\sigma\binom{0010}{0010}$, $\sigma\binom{0100}{0100}$, $\sigma\binom{0200}{0200}$ and $\sigma\binom{0200}{2000}$. This is done for a number of nonspherical potentials, namely for single-P_1, single-P_2, dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions. A number of additional approximations is used to obtain approximate relations between some of these cross sections and to derive a approximate law of corresponding states. A simple model is described which makes the approximate evaluation of collision cross sections for multipole-multipole interactions very straightforward.

1. Introduction

The number of transport and relaxation phenomena in dilute polyatomic gases that has been theoretically elucidated by the use of the Waldmann-Snider equation[1,2] has steadily increased in the past decade[3]. The results of all such treatments are expressed in terms of collision integrals, i.e., of matrix elements of the Waldmann-Snider collision superoperator. Although some work already has been done on the connection between such collision integrals and the nonspherical intermolecular potential[4], many questions remain unanswered. It is the purpose of the present article to derive a number of expressions for certain collision integrals which are as exact as possible (for linear molecules). From these formulae a number of more approximate expressions are then derived by means of various (approximate) simplifications. For a list of the various subjects treated in this article, see the Summary (Section 6).

The collision integrals treated in this article will now be discussed in their relation to experiment.

α) The collision cross section $\sigma\binom{0010}{0010}$ determines the bulk viscosity η_V of the gas through the equation[5]

$$\eta_V = k\,T\,[\sigma\binom{0010}{0010}\,\langle v_{\rm rel}\rangle_0\,\{{}^3/_2 + {}^9/_2\,(k/c_{\rm int}) + {}^{27}/_8\,(k/c_{\rm int})^2\}]^{-1}\,, \quad (1.1)$$

where $\langle v_{\rm rel}\rangle_0$ is an average relative velocity equal to $(16\,k\,T/\pi m)^{1/2}$ and $c_{\rm int}$ is the internal heat capacity per molecule.

β) The collision cross section $\sigma\binom{0200}{0200}$ determines the H/p (magnetic field divided by pressure) value for which the Senftleben-Beenakker effect $\Delta\eta_3/\eta_0$ reaches half of its saturation value. Here η_3 is one of the shear viscosity coefficients of the De Groot-Mazur scheme[6] and η_0 is the field-free shear viscosity coefficient. The relation mentioned above is given as[7]

$$(H/p)_{\frac{1}{2}\cdot\eta_3} = \hbar\langle v_{\rm rel}\rangle_0\,\sigma\binom{0200}{0200}\,[g_{\rm rot}\,\mu_{\rm N}\,k\,T]^{-1}\,, \quad (1.2)$$

where $g_{\rm rot}$ is the rotational g-factor and $\mu_{\rm N}$ the nuclear magneton.

γ) The collision cross section $\sigma\binom{0200}{2000}$ determines the saturation value of $\Delta\eta_3/\eta_0$ via the relation[7]

$$(\Delta\eta_3/\eta_0)_{\rm sat} = -\,\sigma^2\binom{0200}{2000}\,[\sigma\binom{0200}{0200}\,\sigma\binom{2000}{2000}]^{-1}\,, \quad (1.3)$$

with $\sigma\binom{2000}{2000}$ related to η_0 by[7]

$$\eta_0 = k\,T\,[\langle v_{\rm rel}\rangle_0\,\sigma\binom{2000}{2000}]^{-1}\,. \quad (1.4)$$

δ) The collision integrals $\sigma\binom{0100}{0100}'$ and $\sigma\binom{0200}{0200}'$ occur in the theory of nuclear magnetic resonance in diatomic gases. See Refs. 8 and 9.

ε) The cross section $\sigma\binom{0100}{0100}$ does not enter into the theory of any easily measurable phenomenon (for one example, see Ref. [10]). It has been included here for completeness.

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2. Derivation of General Expressions for Diagonal Collision Integrals

The general expression for a collision integral as derived from the Waldmann-Snider equation reduces somewhat if the collision integral is diagonal. It is in that case given by[11]

$$(\mathbf{A}, \mathscr{R}\,\mathbf{A}) = (2\,\pi)^4\,\hbar^2\,\mathrm{tr}_1\,\mathrm{tr}_2 \iiiint f_1{}^{(0)}\,f_2{}^{(0)}\,\mathbf{A}_1{}^{t\dagger}\{(\mathbf{A}_1+\mathbf{A}_2)\,t^g{}_{g'}\,t_{g'}{}^{g\dagger} \\ - t^g{}_{g'}\,(\mathbf{A}_1{}'+\mathbf{A}_2{}')\,t_{g'}{}^{g\dagger}\}\,\delta(E)\,\delta(P)\,\mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2\,\mathrm{d}\boldsymbol{p}_1{}'\,\mathrm{d}\boldsymbol{p}_2{}'\,. \tag{2.1}$$

Here, $t_{g'}{}^g$ and $t_{g'}{}^{g\dagger}$ are matrix elements of the transition operator $\mathbf{t}$ and its adjoint, respectively, in (relative) momentum space, $\boldsymbol{g}$ and $\boldsymbol{g}'$ denoting the relative velocities before and after a collision. These matrix elements are still operators in internal state space. A prime indicates a dependence on $\boldsymbol{p}_1{}'$ and $\boldsymbol{p}_2{}'$, the postcollisional, rather than on $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$, the precollisional linear momenta of the colliding molecules. The Dirac delta functions express the conservation of total linear momentum and total energy, while the symbols tr_1 and tr_2 indicate that the traces over internal states of the two molecules are to be performed. The superscript ,,t“ denotes a tensorial transpose, while the dagger (†) indicates the Hermitean conjugate. The equilibrium distribution function, $f^{(0)}$, is, for linear molecules, given by

$$f_j{}^{(0)} = Q^{-1}\,g(j)\exp\{-B\,j(j+1)\}\,h^{(0)}\,, \qquad h^{(0)} = (2\,\pi\,m\,k\,T)^{-3/2}\exp(-W^2)\,, \tag{2.2}$$

where $g(j)$ is the weight of level j due to nuclear spin states [e.g., $g(2k)=1$ and $g(2k+1)=3$ for normal hydrogen], $B=\hbar^2/(2\,I\,k\,T)$ with I the moment of inertia of the molecule,

$$Q = \textstyle\sum_j g(j)\,(2j+1)\exp\{-B\,j(j+1)\}$$

is the rotational partition function and $\boldsymbol{W}$ is the reduced peculiar velocity, $\boldsymbol{W}=\boldsymbol{p}/(2\,m\,k\,T)^{1/2}$.

The form of the transition operator $\mathbf{t}$ in the first order distorted wave Born approximation (DWBA) has already been discussed in the literature[4, 11, 12, 13–15].

The result may be summarized as follows: for a potential of the form (see refs.[13–15] for the Cartesian tensor notation)

$$V(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{r}}_2, \boldsymbol{R}) = \sum_{l_1, l_2, L} V_{l_1 l_2 L}(R)\,[\hat{\boldsymbol{r}}_1]^{(l_1)}\,[\hat{\boldsymbol{r}}_2]^{(l_2)} \odot^{l_1+l_2} \mathbf{T}(l_1, l_2, L) \odot^L [\hat{\boldsymbol{R}}]^{(L)}\,, \tag{2.3}$$

the DWBA transition operator has the form

$$t^g{}_{g'} = \sum_{l_1, l_2, L} t^g{}_{g'}(l_1, l_2, L)\,, \tag{2.4}$$

$$t^g{}_{g'}(l_1, l_2, L) = [\hat{\boldsymbol{r}}_1]^{(l_1)}\,[\hat{\boldsymbol{r}}_2]^{(l_2)} \odot^{l_1+l_2} \mathbf{T}(l_1, l_2, L) \odot^L \mathbf{A}^{(L)}{}_{l_1 l_2}(\mathbf{g}, \mathbf{g}')\,. \tag{2.5}$$

In these equations $\hat{\boldsymbol{r}}_i$ is the unit vector along the internuclear axis of the i-th molecule, while $\boldsymbol{R}$ (absolute value R, $\hat{\boldsymbol{R}}=\boldsymbol{R}/R$) is the vector extending from the center-of-mass of molecule 1 to the center-of-mass of molecule 2. Further, $\mathbf{T}(l_1, l_2, L)$ is a Cartesian $(3-j)$-tensor[15], while the symbol $\odot^k$ indicates a k-fold contraction. The L-th rank tensor $A^{(L)}{}_{l_1 l_2}(\boldsymbol{g}, \boldsymbol{g}')$ is given by [for $(l_1, l_2, L) \neq (0, 0, 0)$]:

$$\mathbf{A}^{(L)}{}_{l_1 l_2}(\boldsymbol{g}, \boldsymbol{g}') = \int \mathrm{d}\boldsymbol{R}\,\chi^{(+)}{}_{-\boldsymbol{k}}(\mathbf{R})\,V_{l_1 l_2 L}(R)\,[\hat{\boldsymbol{R}}]^{(L)}\,\chi^{(+)}{}_{\boldsymbol{k}'}(\mathbf{R})\,. \tag{2.6}$$

Here, $\chi^{(+)}{}_{\boldsymbol{k}}(\boldsymbol{R})$ is the solution of the Schrödinger equation for the spherical part $V_0(R)\,[\equiv V_{000}(R)]$ of the intermolecular potential determined by the plane wave $h^{-3/2}\exp\{i\,\boldsymbol{k}\cdot\boldsymbol{R}\}$ and the outgoing scattering condition. The wavevector $\boldsymbol{k}$ is related to the relative velocity $\boldsymbol{g}$ by

$$\boldsymbol{k} = \tfrac{1}{2}\,m\,\mathbf{g}/\hbar\,. \tag{2.7}$$

It is convenient to define ,,matrix elements“ of collision integrals between sets of ,,potential quantum numbers“ (l_1, l_2, L) by the equation

$$\langle l_1 l_2 L|\,(\mathbf{A}, \mathscr{R}\,\mathbf{A})\,|l_1{}'\,l_2{}'\,L'\rangle = (2\,\pi)^4\,\hbar^2\,\mathrm{tr}_1\,\mathrm{tr}_2 \iiiint f_1{}^{(0)}\,f_2{}^{(0)}\,\mathbf{A}_1{}^{t\dagger} \\ \times\{(\mathbf{A}_1+\mathbf{A}_2)\,t^g{}_{g'}(l_1, l_2, L)\,t_{g'}{}^{g\dagger}(l_1{}', l_2{}', L') - t^g{}_{g'}(l_1, l_2, L)\,(\mathbf{A}_1{}'+\mathbf{A}_2{}')\,t_{g'}{}^{g\dagger}(l_1{}', l_2{}', L')\}\,\delta(E)\,\delta(P) \\ \times\,\mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2\,\mathrm{d}\boldsymbol{p}_1{}'\,\mathrm{d}\boldsymbol{p}_2{}'\,. \tag{2.8}$$

In what follows only ,,diagonal in potential,, matrix elements, i.e., matrix elements with $(l_1, l_2, L) = (l_1', l_2', L')$, will be considered, the reason being that for the potentials of interest here no cross terms occur (see Section 3 for a discussion on this point).

It is now possible to consider the various collision integrals of interest in this article in detail.

a) *The collision integral* $\left[\begin{smallmatrix}0010\\0010\end{smallmatrix}\right]$.

This collision integral is equal[11] to $\left[\begin{smallmatrix}0001\\0001\end{smallmatrix}\right]$ for which $A = J^2 = j(j+1)$. Inserting this and Eq. (2.5) into Eq. (2.8) yields after some calculation

$$\langle l_1 l_2 L |\left[\begin{smallmatrix}0010\\0010\end{smallmatrix}\right]| l_1 l_2 L\rangle = \Omega(l_1, l_2, L)\, B\, Q^{-2} \sum_{j_1, j_1', j_2, j_2'} g(j_1)\, g(j_2)\, B^{(l_1)}{}_{j_1 j_1'} B^{(l_2)}{}_{j_2 j_2'} j_1(j_1+1)\, \varepsilon \exp(-E)\, \sigma_{l_1 l_2 L}(\varepsilon)\, \langle v_{\mathrm{rel}}\rangle \tag{2.9}$$

Here $\Omega(l_1, l_2, L)$ is the contracted square of $\mathbf{T}(l_1, l_2, L)$ (see Appendix A), while $B^{(l)}_{jj'}$ is defined by ($\mathrm{tr}_{\mathrm{deg}}$ indicates a trace over degenerate internal states)

$$\mathrm{tr}_{\mathrm{deg}}\{\mathscr{P}_j [\hat{\boldsymbol{r}}]^{(l)} \mathscr{P}_{j'} [\hat{\boldsymbol{r}}]^{(l)}\} = B^{(l)}{}_{jj'}\, \mathbf{T}(l, 0, l)\,. \tag{2.10}$$

Further, ε and E are given by

$$\varepsilon = B[j_1(j_1+1) + j_2(j_2+1) - j_1'(j_1'+1) - j_2'(j_2'+1)] \tag{2.11}$$

and

$$E = B[j_1(j_1+1) + j_2(j_2+1)]\,, \tag{2.12}$$

while the cross section $\sigma_{l_1 l_2 L}(\varepsilon)$ has been defined by

$$\sigma_{l_1 l_2 L}(\varepsilon) = \frac{(2\pi)^4 \hbar^2}{\langle v_{\mathrm{rel}}\rangle_0 (2L+1)} \iiiint h_1{}^{(0)} h_2{}^{(0)}\, \mathbf{A}^{(L)}{}_{l_1 l_2}(\boldsymbol{g}, \boldsymbol{g}') \odot^L \mathbf{A}^{(L)*}{}_{l_1 l_2}(\boldsymbol{g}, \boldsymbol{g}')\, \delta(E)\, \delta(P)\, \mathrm{d}\boldsymbol{p}_1 \mathrm{d}\boldsymbol{p}_2 \mathrm{d}\boldsymbol{p}_1' \mathrm{d}\boldsymbol{p}_2'\,. \tag{2.13}$$

The projection operators $\mathscr{P}_j$ occurring in Eq. (2.10) project onto the $(2j+1)$-dimensional manifold of degenerate states belonging to the quantum number j and have been introduced by the indentity

$$[\hat{\boldsymbol{r}}]^{(l)} = \sum_{j, j'} \mathscr{P}_j [\hat{\boldsymbol{r}}]^{(l)} \mathscr{P}_{j'}\,. \tag{2.14}$$

The quantity $B^{(l)}{}_{jj'}$ is given in Appendix A together with the derivation of Eq. (2.10).

b) The collision integrals $\left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]$ and $\left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]'$.

These collision integrals are defined by

$$\left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]^{(\prime)} = \tfrac{1}{3}(\boldsymbol{J} \cdot R^{(\prime)} \boldsymbol{J})\,. \tag{2.15}$$

The collision integral containing $\mathscr{R}'$ is obtained from Eq. (2.1) by dropping the terms $\mathbf{A}_2$ and $\mathbf{A}_2'$ from it. Using the methods sketched in Appendix A, a general result for the collision integrals $\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right]^{(\prime)}$, defined by

$$\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right]^{(\prime)} = ([\boldsymbol{J}]^{(k)} \odot^k, R^{(\prime)} [\boldsymbol{J}]^{(k)})/(2k+1) \tag{2.16}$$

may be derived. This is given as

$$\begin{aligned}\langle l_1 l_2 L |\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right]'| l_1 l_2 L\rangle &= \Omega(l_1, l_2, L)\, [(2k+1)\, Q^2]^{-1} \sum_{j_1, j_1', j_2, j_2'} g(j_1)\, g(j_2)\, B^{(l_1)}{}_{j_1 j_1'} B^{(l_2)}{}_{j_2 j_2'} \\ &\times \left[[\boldsymbol{J}_1]^{(k)} \odot^k [\boldsymbol{J}_1]^{(k)} - \begin{Bmatrix} l_1 & j_1' & j_1 \\ k & j_1 & j_1' \end{Bmatrix} \frac{\alpha^{(k)}{}_{j_1} \alpha^{(k)}{}_{j_1'}}{\alpha^{(0)}{}_{j_1} \alpha^{(0)}{}_{j_1'}} \{\Omega(j_1, k, j_1)\, \Omega(j_1', k, j_1')\}^{1/2} \right] \\ &\times \exp(-E)\, \sigma_{l_1 l_2 L}(\varepsilon)\, \langle v_{\mathrm{rel}}\rangle_0 .\end{aligned} \tag{2.17}$$

and

$$\begin{aligned}\langle l_1 l_2 L |\left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right] - \left[\begin{smallmatrix}0k00\\0k00\end{smallmatrix}\right]'| l_1 l_2 L\rangle &= \Omega(l_1, l_2, L)\, [(2k+1)\, Q^2]^{-1} (-1)^k (2l_1+1)(2l_2+1) \\ &\times \begin{Bmatrix} L & l_1 & l_2 \\ k & l_2 & l_1 \end{Bmatrix} \sum_{j_1, j_2, j_1', j_2'} g(j_1)\, g(j_2)\, B^{(l_1)}{}_{j_1 j_1'} B^{(l_2)}{}_{j_2 j_2'} (\alpha_{j'}{}^{(k)}/\alpha_{j'}{}^{(0)})\, \Omega^{1/2}(j_1, k, j_1) \begin{Bmatrix} j_1' & j_1 & l_1 \\ k & l_1 & j_1 \end{Bmatrix} \\ &\times \left[\alpha_{j_2}{}^{(k)}/\alpha_{j_2}{}^{(0)})\, \Omega^{1/2}(j_2, k, j_2) \begin{Bmatrix} j_2' & j_2 & l_2 \\ k & l_2 & j_2 \end{Bmatrix} - (-1)^k (\alpha_{j_2'}{}^{(k)}/\alpha_{j_2'}{}^{(0)})\, \Omega^{1/2}(j_2', k, j_2') \begin{Bmatrix} j_2 & j_2' & jl_2 \\ k & l_2 & j_2' \end{Bmatrix} \right] \\ &\times \exp(-E)\, \sigma_{l_1 l_2 L}(E)\, \langle v_{\mathrm{rel}}\rangle_0 .\end{aligned} \tag{2.18}$$

In these equations, the $\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$ are $(6-j)$-symbols, while the $\alpha_j^{(k)}$ are discussed in Appendix A.

For the special value $k=1$ a further calculation, using the explicit form of the $\alpha_j^{(k)}$, the $\Omega(j,k,l)$ and the $(6-j)$-symbols gives the results

$$\langle l_1 l_2 L | \left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]' | l_1 l_2 L\rangle = \tfrac{1}{6}\,\Omega(l_1, l_2, L)\, Q^{-2} l_1 (l_1+1)\, S_1 \tag{2.19}$$

and

$$\langle l_1 l_2 L | \left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right] | l_1 l_2 L\rangle = \tfrac{1}{12}\,\Omega(l_1, l_2, L)\, Q^{-2}\{L(L+1) + l_1(l_1+1) - l_2(l_2+1)\}\, S_1 \tag{2.20}$$

with

$$S_1 = \sum_{j_1, j_2, j_1', j_2'} g(j_1)\, g(j_2)\, B^{(l_1)}{}_{j_1 j_1'}\, B^{(l_2)}{}_{j_2 j_2'} \exp(-E)\, \sigma_{l_1 l_2 L}(\varepsilon)\, \langle v_{\text{rel}}\rangle_0 \,. \qquad (2.21$$

From Eqs. (2.19) and (2.20) the interesting relation (see Section 3 for special cases)

$$\begin{aligned} \langle l_1 l_2 L | \left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]' | l_1 l_2 L\rangle + \langle l_2 l_1 L | \left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right]' | l_2 l_1 L\rangle &= [l_1(l_1+1) + l_2(l_2+1)]\,[L(L+1)]^{-1} \\ &\times \{\langle l_1 l_2 L | \left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right] | l_1 l_2 L\rangle + \langle l_2 l_1 L | \left[\begin{smallmatrix}0100\\0100\end{smallmatrix}\right] | l_2 l_1 L\rangle\} \end{aligned} \tag{2.22}$$

is easily derived.

c) The collision integrals $\left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]$ and $\left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]'$.

From Eqs. (2.17) and (2.18) it follows that

$$\begin{aligned} \langle l_1 l_2 L | \left[\begin{smallmatrix}0200\\0200\end{smallmatrix}\right]^{(\prime)} | l_1 l_2 L\rangle &= (1/60)\, \Omega(l_1, l_2, L)\, Q^{-2} \sum_{j_1, j_2, j_1', j_2'} g(j_1)\, g(j_2)\, B^{(l_1)}{}_{j_1 j_1'}\, B^{(l_2)}{}_{j_2 j_2'} \exp(-E) \\ &\times \{3 l_1 (l_1+1)\,[4 j_1^2 + 4 j_1 - (l_1^2 + l_1 + 1)] + \Delta_1^2 + M^{(\prime)}(l_1, l_2, L)\, \Delta_1 \Delta_2\}\, \sigma_{l_1 l_2 L}(\varepsilon)\, \langle v_{\text{rel}}\rangle_0 \,. \end{aligned} \tag{2.23}$$

Here the Δ_i and the $M^{(\prime)}(l_1, l_2, L)$ are given by

$$\Delta_i = j_i(j_i+1) - j_i'(j_i'+1)\,, \tag{2.24}$$

$$\begin{aligned} M(l_1, l_2, L) &= \tfrac{1}{2}[3X(X-1) - \\ &- 4 l_1(l_1+1)\, l_2(l_2+1)]\,[l_1(l_1+1) + l_2(l_2+1)]^{-1} \end{aligned} \tag{2.25}$$

with

$$X = l_1(l_1+1) + l_2(l_2+1) - L(L+1) \tag{2.26}$$

and

$$M'(l_1, l_2, L) = 0\,. \tag{2.27}$$

Equations (2.9), (2.19–21) and 2.23) are the basic formulae from which a calculation of these collision integrals has to be started. It will now be necessary to have a closer look at the cross section $\sigma_{l_1 l_2 L}(\varepsilon)$, in which the collision integrals have been expressed. The starting point for this is eq. (2.6). The scattering wave functions $\chi^{(+)}(\boldsymbol{R})$ occurring there may be expanded in partial waves in the standard way; in Cartesian tensor notation this expansion takes the form

$$\chi_{\boldsymbol{k}}^{(+)}(\boldsymbol{R}) = h^{-3/2} \sum_{m=0}^{\infty} \alpha_m R^{-1} y_m(k|R)\, [\boldsymbol{k}^{\wedge}]^{(m)} \odot^m [\boldsymbol{R}^{\wedge}]^{(m)} \tag{2.29}$$

with

$$\alpha_m = [(2m+1)!/k\, 2^m (m!)^2]\, i^m \exp(i\,\eta_m)\,, \tag{2.29}$$

where η_m is the phase shift. α_m has been chosen so that y_m has the asymptotic form

$$y_m(k|R) \underset{R\to\infty}{\approx} \sin(kR - \tfrac{1}{2} m x + \eta_m)\,.$$

Insertion of this expansion in Eq. (2.6) yields (using the results of Appendix A)

$$\begin{aligned} \mathbf{A}_{l_1 l_2}^{(L)}(\mathbf{g}, \mathbf{g}') &= h^{-3} \sum \alpha_{m_1} \alpha_{m_2} (-1)^{m_1}\, \beta_{l_1 l_2 L}^{m_1 m_2}(\gamma, \gamma') \\ &\times \mu(m_1, L, m_2) \\ &\times [\boldsymbol{\gamma}^{\wedge}]^{(m_1)} \odot^{m_2} \mathbf{T}(m_1, L, m_2) \odot^{m_1} [\boldsymbol{\gamma}'^{\wedge}]^{(m_2)}\,, \end{aligned} \tag{2.30}$$

where instead of $\boldsymbol{k}$ or $\boldsymbol{g}$ the dimensionsless vector $\boldsymbol{\gamma}$ has been introduced by the relation

$$\boldsymbol{\gamma} = \hbar\, (m\, k T)^{-1/2}\, \boldsymbol{k}\,. \tag{2.31}$$

The quantities $\beta_{l_1 l_2 L}^{m_1 m_2}(\gamma, \gamma')$ are given by

$$\beta_{l_1 l_2 L}^{m_1 m_2}(\gamma, \gamma') = \int \mathrm{dR}\, y_{m_1}(k|R)\, V_{l_1 l_2 L}(R)\, y_{m_2}(k'|R)\,. \tag{2.32}$$

Equation (2.30) may be inserted into Eq. (2.13). After changing the integration variables from the $\boldsymbol{p}$'s to $\boldsymbol{\gamma}$, $\boldsymbol{\gamma}'$ and the dimensionless center-of-mass velocity $\boldsymbol{G}$ by means of the transformation (see the definition following Eq. (2.2) for $\boldsymbol{W}$)

$$\begin{aligned} &\boldsymbol{W}_1 = 2^{-1/2}(\boldsymbol{G} - \boldsymbol{\gamma}); \quad \boldsymbol{W}_2 = 2^{-1/2}(\boldsymbol{G} + \boldsymbol{\gamma}); \\ &\boldsymbol{W}_1' = 2^{-1/2}(\boldsymbol{G} - \boldsymbol{\gamma}'); \quad \boldsymbol{W}_2' = 2^{-1/2}(\boldsymbol{G} + \boldsymbol{\gamma}'), \end{aligned} \tag{2.33}$$

a number of integrations may be performed with the final result

$$\sigma_{l_1 l_2 L}(\varepsilon) = \int_0^{\infty} \mathrm{d}\gamma\, \gamma^2 \gamma'\, H_{l_1 l_2 L}(\gamma, \gamma')\, \mathrm{e}^{-\gamma^2}, \tag{2.34}$$

$$H_{l_1 l_2 L}(\gamma,\gamma') = m^2 [32\pi^3 \hbar^4 (2L+1)]^{-1} \times \sum_{m_1,m_2} |\alpha_{m_1}|^2 |\alpha_{m_2}|^2 \mu^2(m_1,L,m_2) \times \mu(m_1,0,m_2)\,\mu(m_2,0,m_2)\,\Omega(m_1,L,m_2) \times |\beta^{m_1 m_2}_{l_1 l_2 L}(\gamma,\gamma')|^2 . \tag{2.35}$$

It is now in principle possible to completely calculate a collision integral, the necessary steps being:

a) Solve the partial wave equations for $V_0(R)$.

b) Use these solutions to calculate the $\beta^{m_1 m_2}_{l_1 l_2 L}(\gamma,\gamma')$ and $H_{l_1 l_2 L}(\gamma,\gamma')$.

c) Calculate $\sigma_{l_1 l_2 L}(\varepsilon)$ and from this the collision integrals using Eqs. (2.9), (2.19—21) and (2.23).

Step c) may be simplified by making use of the following symmetry property: since [see Eq. (2.32)]

$$\beta^{m_1 m_2}_{l_1 l_2 L}(\gamma,\gamma') = \beta^{\overline{m_1 m_2}}_{l_1 l_2 L}(\gamma',\gamma) \tag{2.36}$$

it follows that [see Eq. (2.35)]

$$H_{l_1 l_2 L}(\gamma,\gamma') = H_{l_1 l_2 L}(\gamma',\gamma) . \tag{2.37}$$

Further, energy conservation requires that $\gamma'^2 = \gamma^2 + \varepsilon$, so that if $\varepsilon < 0$ the integral in Eq. (2.34) does not really have zero as its lower limit, but $(-\varepsilon)^{1/2}$. Using this and the symmetry relation (2.37) it is easily shown that the functional dependence of $\sigma_{l_1 l_2 L}(\varepsilon)$ may be represented by

$$\sigma_{l_1 l_2 L}(\varepsilon) = \exp(\varepsilon/2)\, I_{l_1 l_2 L}(|\varepsilon|) . \tag{2.38}$$

This equation has been used in the next section to simplify the expressions for the collision integrals for specific potentials.

Instead of the collision integrals themselves, the collision cross sections which may be derived from them[16] have been used in what follows. The definitions of these cross sections for the cases of interest here are[16]

$$\begin{aligned} \sigma\binom{0010}{0010} &= \tfrac{2}{3} \langle v_{\mathrm{rel}} \rangle_0^{-1} \left[{0010 \atop 0010}\right] , \\ \sigma\binom{0100}{0100}^{(\prime)} &= 3 [\langle J^2 \rangle_0 \langle v_{\mathrm{rel}} \rangle_0]^{-1} \left[{0100 \atop 0100}\right]^{(\prime)} , \\ \sigma\binom{0200}{0200}^{(\prime)} &= \tfrac{15}{2} [\langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0 \langle v_{\mathrm{rel}} \rangle_0]^{-1} \left[{0200 \atop 0200}\right]^{(\prime)} . \end{aligned} \tag{2.39}$$

3. Expressions for a Number of Potentials

From the general formulae for the diagonal cross sections derived in the previous section expressions for particular potentials may be extracted. To this end it is only necessary to consider the various possible values that j_1' and j_2' can take, given values of j_1 and j_2. For the potentials considered in this section, these selection rules are listed in Table I. They may all be obtained from the factor $\mu(j_1, l_1, j_1')\,\mu(j_2, l_2, j_2')$ occurring in each collision integral (Appendix A). This factor is zero unless the indices satisfy certain conditions given in Appendix A. The procedure for finding an expression for a certain potential is then very straightforward: the different types of collisions which may contribute are classified using Table I, then the known factors occurring in Eqs. (2.9), (2.19—21) and (2.23) are worked out for those values of j_1' and j_2' and finally all parts are gathered together, using also Eqs. (2.38) and (2.39).

Table 1. Selection Rules for Molecular Collisions.

Potential quantum numbers			Potential Symbol	Δj_1	Δj_2
l_1	l_2	L			
0	0	0	SPH	0	0
1	0	1	P1	± 1	0
0	1	1		0	± 1
2	0	2	P2	$0, \pm 2$	0
0	2	2		0	$0, \pm 2$
1	1	2	DD	± 1	± 1
1	2	3	DQ	± 1	$0, \pm 2$
2	1	3		$0, \pm 2$	± 1
2	2	4	QQ	$0, \pm 2$	$0, \pm 2$

The expressions so obtained are certainly useful if one of the types of potential listed in Table I is dominant. If more than one type of potential has to be included, cross terms, i.e., matrix elements nondiagonal in potential quantum numbers, might be expected to occur. It may be shown quite generally (in the same way as the expressions in the previous section were derived) that $\sigma\binom{0010}{0010}$, $\sigma\binom{0100}{0100}$, $\sigma\binom{0100}{0100}'$ and $\sigma\binom{0200}{0200}'$ are strictly diagonal in potential quantum numbers and that $\sigma\binom{0200}{0200}$ is diagonal in the restricted set of Table I.

In the following pages, the results for several potentials are listed. In order to make reference to these equations easier, a special numbering system is used, which includes the potential symbol (see Table I for these). Explicit expressions for the dipole-quadrupole and quadrupole-quadrupole interactions have also been obtained. These are not listed here because they are too lengthy.

Also listed are expressions in the high temperature approximation. In this approximation $I_{l_1 l_2 L}(\varepsilon)$ is replaced by $I_{l_1 l_2 L}(\langle \varepsilon \rangle_0)$. The remaining sums are then calculated in the classical limit, i.e., they are replaced by integrals. Thr averages needed to compute $\langle\varepsilon\rangle_0$ are:

$$\begin{aligned}\langle j\rangle_0 &= \tfrac{1}{2}(\pi/B)^{1/2}\,,\\ \langle|j_1-j_2|\rangle_0 &= \tfrac{1}{2}(2-\sqrt{2})\,(\pi/B)^{1/2}\,,\\ \langle|j_1-2j_2|\rangle_0 &= \tfrac{1}{2}(3-{}^{24}/_{25}\sqrt{5})\,(\pi/B)^{1/2}\,.\end{aligned} \qquad (3.1)$$

In all expressions obtained only the lowest power of B is retained. The high temperture approximation is expected to be rather good since ε is proportional to T^{-1}, i.e., at high temperatures the dependence of $I_{l_1 l_2 L}(\varepsilon)$ on ε is weak. Therefore replacement of ε by its average value will be reasonable for many values of j..

A) *Single-P_1 potential* (P1)

a) Exact DWBA expressions:

$$\sigma\binom{0010}{0010} = (8/3)\,B^2\,Q^{-1}\sum_{j=0}^{\infty}(j+1)^3 \times \exp[-B(j+1)^2]\,I_{101}\{2B(j+1)\}\,. \qquad \text{(P1-1)}$$

$$\sigma\binom{0100}{0100} = 2\,[Q\langle J^2\rangle_0]^{-1}\sum_{j=0}^{\infty}(j+1) \times \exp[-B(j+1)^2]\,I_{101}\{2B(j+1)\}\,. \qquad \text{(P1-2)}$$

$$\sigma\binom{0200}{0200} = \tfrac{1}{2}\,[Q\langle J^2(J^2-\tfrac{3}{4})\rangle_0]^{-1} \times \sum_{j=0}^{\infty}(j+1)\,(14j^2+28j+5) \times \exp[-B(j+1)^2]\,I_{101}\{2B(j+1)\}\,. \qquad \text{(P1-3)}$$

$$\sigma\binom{0200}{0200} = \tfrac{21}{8}\,[B^2\langle J^2(J^2-\tfrac{3}{4})\rangle_0]^{-1}\,\sigma\binom{0010}{0010} - (9/4)\,\langle J^2\rangle_0\,\langle J^2(J^2-\tfrac{3}{4})\rangle_0^{-1}\,\sigma\binom{0100}{0100}\,. \qquad \text{(P1-3a)}$$

b) High temperature expressions:

$$\sigma\binom{0010}{0010} = (\tfrac{4}{3})\,B\,I_{101}(\sqrt{\pi}\,B)\,. \qquad \text{(P1-4)}$$

$$\sigma\binom{0100}{0100} = B\,I_{101}(\sqrt{\pi}\,B)\,. \qquad \text{(P1-5)}$$

$$\sigma\binom{0200}{0200} = (\tfrac{7}{4})\,B\,I_{101}(\sqrt{\pi}\,B)\,. \qquad \text{(P1-6}$$

B) *Single-P_2 potential* (P2)

a) Exact DWBA expressions:

$$\sigma\binom{0010}{0010} = (8/3)\,B^2\,Q^{-1}\sum_{j=0}^{\infty}g(j)\,(j+1)\,(j+2)\,(2j+3)\,\exp\{-B(j^2+3j+3)\}\,I_{202}\{2B(2j+3)\}\,. \qquad \text{(P2-1)}$$

$$\sigma\binom{0100}{0100} = 2\,[Q\langle J^2\rangle_0]^{-1}\left[Q\left\langle\frac{j(j+1)}{(2j-1)\,(2j+3)}\right\rangle_0 I_{202}(0) + 3\sum_{j=0}^{\infty}g(j)\,\frac{(j+1)\,(j+2)}{2j+3}\,\exp\{-B(j^2+3j+3)\}\,I_{202}\,\{2B(2j+3)\}\,.\right] \qquad \text{(P2-2)}$$

$$\sigma\binom{0200}{0200} = \tfrac{1}{2}\,[Q\langle J^2(J^2-\tfrac{3}{4})\rangle_0]^{-1}\left[3\,Q\left\langle(4j^2+4j-7)\,\frac{j(j+1)}{(2j-1)\,(2j+3)}\right\rangle_0 I_{202}(0) + 3\sum_{j=0}^{\infty}g(j)\,\frac{(j+1)\,(j+2)}{2j+3}\,\exp\{-B(j^2+3j+3)\}(44j^2+132j+62)\,I_{202}\{2B(2j+3)\}\right]. \qquad \text{(P2-3)}$$

b) High temperature expressions:

$$\sigma\binom{0010}{0010} = (8/3)\,B\,I_{202}(2\sqrt{\pi}\,B)\,, \qquad \text{(P2-4)}$$

$$\sigma\binom{0100}{0100} = \tfrac{1}{2}\,B\,I_{202}(0) + \tfrac{3}{2}\,B\,I_{202}(2\sqrt{\pi}\,B)\,, \qquad \text{(P2-5)}$$

$$\sigma\binom{0200}{0200} = \tfrac{3}{4}\,B\,I_{202}(0) + \tfrac{11}{4}\,B\,I_{202}(2\sqrt{\pi}\,B)\,. \qquad \text{(P2-6)}$$

Note that Eqs. (P2-4) and (P2-6) are identical with the expressions for these cross sections derived in Ref. [11] by a different, more approximate method. The correspondence is seen when the identifications

$$B\,I_{202}(0) = \sigma^{(0)} \quad\text{and}\quad I_{202}(2\sqrt{\pi}\,B)/I_{202}(0) = \alpha$$

are made.

C) *The Dipole-Dipole interaction* (*DD*)

a) Exact DWBA expressions:

$$\sigma\binom{0010}{0010} = \left(\tfrac{20}{27}\right) B^2 Q^{-2} \sum_{j_1, j_2=0}^{\infty} (j_1+1)(j_2+1) \exp\left[-B\{(j_1+1)^2+(j_2+1)^2\}\right] \times \left[(j_1+j_2+2)^2 I_{112}\{2B(j_1+j_2+2)\} + (j_1-j_2)^2 I_{112}\{2B|j_1-j_2|\}\right]. \tag{DD-1}$$

$$\sigma\binom{0100}{0100} = \left[\tfrac{5}{3}\right] \left[Q^2 \langle J^2 \rangle_0\right]^{-1} \sum_{j_1, j_2=0}^{\infty} (j_1+1)(j_2+1) \exp\left[-B\{(j_1+1)^2+(j_2+1)^2\}\right] \times \left[I_{112}\{2B(j_1+j_2+2)\} + I_{112}\{2B|j_1-j_2|\}\right]. \tag{DD-2}$$

$$\sigma\binom{0100}{0100}' = \tfrac{1}{3}\, \sigma\binom{0100}{0100}. \tag{DD-2a}$$

$$\sigma\binom{0200}{0200}^{(\prime)} = \left(\tfrac{5}{36}\right) \left[Q^2 \langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0\right]^{-1} \sum_{j_1, j_2=0}^{\infty} (j_1+1)(j_2+1) \exp\left[-B\{(j_1+1)^2+(j_2+1)^2\}\right] \times \left[2(14 j_1^2 + 28 j_1 + 5) \{I_{112}\{2B(j_1+j_2+2)\} + I_{112}\{2B|j_1-j_2\}\} + \delta^{(\prime)} (j_1+1)(j_2+1) \{I_{112}\{2B(j_1+j_2+2)\} - I_{112}\{2B|j_1-j_2)\}\}\right], \quad (\delta = 1,\ \delta' = 0). \tag{DD-3}$$

b) High temperature expressions:

$$\sigma\binom{0010}{0010} = \left(\tfrac{5}{54}\right) B\left[(4+\pi) I_{112}(2\sqrt{\pi B}) + (4-\pi) I_{112}\{(2-\sqrt{2})\sqrt{\pi B}\}\right]. \tag{DD-4}$$

$$\sigma\binom{0100}{0100} = \left(\tfrac{5}{12}\right) B\left[I_{112}(2\sqrt{\pi B}) + I_{112}\{(2-\sqrt{2})\sqrt{\pi B}\}\right]. \tag{DD-5}$$

$$\sigma\binom{0200}{0200}^{(\prime)} = \left(\tfrac{35}{72}\right) B\left[(1 + \delta^{(\prime)} \pi/112) I_{112}(2\sqrt{\pi B}) + (1 - \delta^{(\prime)} \pi/112) I_{112}\{(2-\sqrt{2})\sqrt{\pi B}\}\right]. \tag{DD-6}$$

From the foregoing high temperature expressions, a number of approximate relations between diagonal cross sections may be derived. These are listed in Table II, also for the quadrupole-quadrupole interaction explicit expressions for which have been omitted because of their complexibility.

Table 2. Relations between Diagonal Collision Cross Sections (High Temperature Approximation).

Potential Symbol	Relation
P1	$\sigma\binom{0100}{0100} \cong {}^3/_4\ \sigma\binom{0010}{0010}$
P1	$\sigma\binom{0200}{0200} \cong {}^7/_4\ \sigma\binom{0100}{0100}$
P2	$\sigma\binom{0200}{0200} \cong {}^3/_2\ \sigma\binom{0100}{0100} + {}^3/_{16}\, \sigma\binom{0010}{0010}$
DD	$\sigma\binom{0200}{0200}' \cong {}^7/_4\ \sigma\binom{0100}{0100}'$
DD	$\sigma\binom{0200}{0200} \cong {}^9/_8\ \sigma\binom{0100}{0100} + {}^3/_{64}\, \sigma\binom{0010}{0010}$
QQ	$\sigma\binom{0200}{0200} \cong {}^9/_{10}\, \sigma\binom{0100}{0100} + {}^3/_{32}\, \sigma\binom{0010}{0010}$

4. A Model for the Transition Operator

The program sketched at the end of Section 2 is rather formidable. Therefore it is useful to try and find models for the transition operator which either furnish new relations between collision integrals or make an approximate evaluation of them much simpler. In this section a model transition operator will be described which not only gives a new set of approximate relations, including an approximate law of corresponding states, but may also be specialized (Section 5) to yield rather easily calculable expressions for the contributions to the collision integrals due to multipole-multipole interactions. The starting point of the model is again Eq. (2.6). This expression would be much more useful if the full Born approximation could be used, i.e., if the solutions $\chi_{\boldsymbol{k}}^{(+)}(\boldsymbol{R})$ could be replaced by plane waves. It is now assumed that this is the case, *provided* that the potential $V_{l_1 l_2 L}(R)$ is replaced by another potential, $\hat{V}_{l_1 l_2 L}(R)$. With this assumption, Eq. (2.6) becomes*

$$\mathbf{A}^{(L)}{}_{l_1 l_2}(\boldsymbol{g}, \boldsymbol{g}') = h^{-3} \int \mathrm{d}\boldsymbol{R} \exp(i\boldsymbol{K}\cdot\boldsymbol{R})\, \hat{V}_{l_1 l_2 L}(R) \times [\boldsymbol{R}]^{(L)}, \tag{4.1}$$

where $\boldsymbol{K} = \boldsymbol{k}' - \boldsymbol{k}$. It is furthermore assumed that $\hat{V}_{l_1 l_2 L}(R)$ has the form

$$\hat{V}_{l_1 l_2 L}(R) = C_{l_1 l_2 L} F_{l_1 l_2 L}(R/d_{l_1 l_2 L}), \tag{4.2}$$

---

* It should be noted that Eq. (4.1) is only approximate. There does not in general exist a local $\hat{V}_{l_1 l_2 L}(R)$ such that Eq. (4.1) is exact. It is, however, hoped that Eq. (4.1) is a reasonable approximation for a large range of values of $\boldsymbol{k}$ and $\boldsymbol{k}'$.

where $C_{l_1 l_2 L}$ has the dimension of an energy and $d_{l_1 l_2 L}$ is a length characteristic of $\hat{V}_{l_1 l_2 L}(R)$. Using Eq. (4.2) and the expansion of the plane wave in spherical Bessel functions

$$\exp[i\,\boldsymbol{K}\cdot\boldsymbol{R}] = \sum_{m=0}^{\infty} [(2\,m+1)!/2^m\,(m!)^2] \times \\ \times\, i^m\, j_m(k\,R)\,[\boldsymbol{K}\hat{\ }]^{(m)} \odot^m [\boldsymbol{R}\hat{\ }]^{(m)}\,, \qquad (4.3)$$

the result

$$\mathbf{A}^{(L)}{}_{l_1 l_2}(\mathbf{g},\mathbf{g}') = 4\,\pi\,h^{-3}\,i^L\,C_{l_1 l_2 L} \\ \times\, d^3{}_{l_1 l_2 L}[\boldsymbol{K}\hat{\ }]^{(L)}\,G_{l_1 l_2 L}(\hat{K}\,d_{l_1 l_2 L}) \qquad (4.4)$$

with

$$G_{l_1 l_2 L}(x) = \int_0^{\infty} \mathrm{d}y\,y^2\,j_L(x\,y)\,F_{l_1 l_2 L}(y) \qquad (4.5)$$

is obtained. When Eq. (4.4) is inserted into Eq.(2.12) for $\sigma_{l_1 l_2 L}(\varepsilon)$ and the transformation (2.33) is used, the following result is obtained after some calculation:

$$\sigma_{l_1 l_2 L}(\varepsilon) = \exp(\varepsilon/2)\,I_{l_1 l_2 L}(|\,\varepsilon\,|) \\ = \exp(\varepsilon/2)\,\sigma^{(0)}{}_{l_1 l_2 L}\,I'{}_{l_1 l_2 L}(|\,\varepsilon\,|) \qquad (4.6)$$

with

$$\sigma^{(0)}{}_{l_1 l_2 L} = \pi\,m\,C^2{}_{l_1 l_2 L}\,d^4{}_{l_1 l_2 L}\,2^{L+1}(L!)^2 \\ \times\,[\hbar^2\,k\,T\,(2\,L+1)!]^{-1} \qquad (4.7)$$

and

$$I'{}_{l_1 l_2 L}(|\,\varepsilon\,|) = \int_0^{\infty} \mathrm{d}y\,y\,\{G_{l_1 l_2 L}(y)\}^2 \qquad (4.8) \\ \times\,\exp[-\,\alpha^2\,y^2 - \varepsilon^2/(16\,\alpha^2\,y^2)]\,,$$

where

$$\alpha^2 = \hbar^2/(4\,d^2{}_{l_1 l_2 L}\,m\,k\,T)\,. \qquad (4.9)$$

It is obvious from these equations that now all collision integrals may be approximately calculated if $\hat{V}_{l_1 l_2 L}(R)$ is given. A specific case will be studied in the next section. The *form* (4.4), however, gives rise to a general relation between $\sigma\binom{0010}{0010}$ and $\sigma\binom{0200}{0200}$, the cross section determining the magnitude of the shear viscosity Senftleben-Beenakker effect (see Introduction). This may be seen in the following way. The collision integral $\left[\begin{smallmatrix}0200\\2000\end{smallmatrix}\right]$ is defined by

$$\left[\begin{smallmatrix}0200\\2000\end{smallmatrix}\right] = \tfrac{1}{5}\,([\boldsymbol{J}]^{(2)} : \mathscr{R}\,[\boldsymbol{W}]^{(2)})\,. \qquad (4.10)$$

With the methods of Appendix A and Section 2, this integral may be shown to reduce to

$$\langle l_1\,l_2\,L|\left[\begin{smallmatrix}0200\\2000\end{smallmatrix}\right]|l_1\,l_2\,L\rangle \\ = -\,\tfrac{1}{5}\,\Omega(l_1\,l_2,L)\,(2\,l_1-1)\,(l_1+1)^{-1}\,Q^2 \\ \times \sum_{j_1,j_2,j_1',j_2'} g(j_1)\,g(j_2)\,B^{(l_1)}{}_{j_1 j_1'}\,B^{(l_2)}{}_{j_2 j_2'} \\ \times\,\exp[-\,E]\,j_1(j_1+1)\,\sigma^{(2)}{}_{l_1 l_2 L}(\varepsilon)\,\langle v_{\mathrm{rel}}\rangle_0\,, \qquad (4.11)$$

where $\sigma^{(2)}{}_{l_1 l_2 L}(\varepsilon)$ is given by

$$\sigma^{(2)}{}_{l_1 l_2 L}(\varepsilon) = \frac{(2\,\pi)^4\,\hbar^2\,(1-\delta_{\mathrm{L},0})}{\langle v_{\mathrm{rel}}\rangle_0\,(2\,L+1)} \\ \iiiint \mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2\,\mathrm{d}\boldsymbol{p}_1'\,\mathrm{d}\boldsymbol{p}_2'\,h_1{}^{(0)}\,h_2{}^{(0)}\,\delta(E)\,\delta(P) \qquad (4.12) \\ \times\,(\mathbf{A}^{(L)}{}_{l_1 l_2}(\mathbf{g},\mathbf{g}') \odot^{L-1} \mathbf{A}^{(L)}{}_{l_1 l_2}(\mathbf{g},\mathbf{g}')) : ([\boldsymbol{\gamma}]^{(2)} \\ -\,[\boldsymbol{\gamma}']^{(2)})\,.$$

These equations are exacat in the DWBA. The factor $(1-\delta_{L,0})$ has been inserted to show explicitly that $\sigma^{(2)}{}_{l_1 l_2 L}(\varepsilon)$ is zero if $L=0$. If now the approximate form (4.4) is substituted in Eq. (4.12), the contractions may be performed with the interesting result

$$\sigma^{(2)}{}_{l_1 l_2 L}(\varepsilon) \simeq -\,\frac{1}{3}\,\frac{(L+1)\,(1-\delta_{L,0})}{2\,L-1}\,\varepsilon\,\sigma_{l_1 l_2 L}(\varepsilon)\,. \qquad (4.13)$$

When this is used in Eq. (4.11), a comparison of the resulting expression with Eq. (2.9) shows that

$$\langle l_1\,l_2\,L|\left[\begin{smallmatrix}0200\\2000\end{smallmatrix}\right]|\,l_1\,l_2\,L\rangle \simeq (1/15)\,(1-\delta_{L,0}) \qquad (4.14) \\ \times\,\frac{L+1}{2\,L-1}\,\frac{2\,l_1-1}{l_1+1}\,B^{-1}\,\langle l_1\,l_2\,L|\left[\begin{smallmatrix}0010\\0010\end{smallmatrix}\right]|\,l_1\,l_2\,L\rangle\,.$$

This equation makes it possible to relate diagonal (in potential quantum numbers) matrix elements of $\sigma\binom{0200}{2000}$ to diagonal matrix elements of $\sigma\binom{0010}{0010}$. In particular, the relations listed in Table III are readily obtained, using the definition [16] of $\sigma\binom{0200}{2000}$

$$\sigma\binom{0200}{2000} = (15)^{1/2}\,[\langle J^2\,(J^2-\tfrac{3}{4})\rangle_0{}^{1/2}\,\langle v_{\mathrm{rel}}\rangle_0]^{-1}\left[\begin{smallmatrix}0200\\2000\end{smallmatrix}\right]. \qquad (4.15)$$

In order to derive Eq. (4.13), the full form (4.4) is not really necessary, the tensorial dependence on $[\boldsymbol{K}\hat{\ }]^{(L)}$ being crucial only. Such a tensorial dependence may be derived from much less stringent assumptions than those made in the first part of this section. It is therefore reasonable to expect that the relations of Table III are rather accurate. This is reinforced by the fact that the relation for the single-P_2 potential, which has been derived earlier [11], has been checked rather extensively [5]. Another check can be had by combining the relation for the P_1 potential in Table III with Eqs. (P1-4) and (P1-6), the result being that $\sigma\binom{0200}{0200}$ $(P_1) \simeq 4.8$ $\sigma\binom{0200}{2000}$ (P_1). Köhler[4] has performed a quantum mechanical calculation of both $\sigma\binom{0200}{0200}$ and $\sigma\binom{0200}{2000}$ for the P_1 potential for HD. He finds $\sigma\binom{0200}{0200}$ (P_1) $= 4.7\;\sigma\binom{0200}{2000}$ (P_1), so that the approximation may be said to be excellent in this case.

Table 3. Relations between $\sigma\binom{0200}{2000}$ and $\sigma\binom{0010}{0010}$.

Potential Symbol	$\sigma\binom{0200}{2000}/\sigma\binom{0010}{0010}$	
	From Eq. (4.14)	High temperature form
P1, P2	$(15)^{1/2}\{10\,B\,\langle J^2(J^2-3/4)\rangle_0{}^{1/2}\}^{-1}$	$(30)^{1/2}/20$
DD	$(15)^{1/2}\{20\,B\,\langle J^2(J^2-3/4)\rangle_0{}^{1/2}\}^{-1}$	$(30)^{1/2}/40$
QQ	$(15)^{1/2}\{14\,B\,\langle J^2(J^2-3/4)\rangle_0{}^{1/2}\}^{-1}$	$(30)^{1/2}/28$

The full Born approximation [with $\hat{V}_{l_1 l_2 L}(R)$], with the results (4.6-9), may be used to derive an approximate law of corresponding states for any collision integral. Consider two gases, distinguished by indices A and B. Since all collision integrals depend, in the approximation used, on the temperature only via B, α, and $\sigma^{(0)}{}_{l_1 l_2 L}$, the equality

$$\frac{\langle l_1 l_2 L |\, \sigma\binom{pqst}{p'q's't'}_k \,| l_1 l_2 L\rangle^{\mathrm{A}}(T)}{\sigma^{(0)\mathrm{A}}_{l_1 l_2 L}(T)} = \frac{\langle l_1 l_2 L |\, \sigma\binom{pqst}{p'q's't'}_k \,| l_1 l_2 L\rangle^{\mathrm{B}}(T')}{\sigma^{(0)\mathrm{B}}_{l_1 l_2 L}(T')} \tag{4.16}$$

will be satisfied if T and T' simultaneously satisfy the equations

$$T'/T = I_{\mathrm{A}}/I_{\mathrm{B}} \tag{4.17}$$

and

$$T'/T = (m_{\mathrm{A}}/m_{\mathrm{B}})\,(d^{\mathrm{A}}{}_{l_1 l_2 L}/d^{\mathrm{B}}{}_{l_1 l_2 L})^2\,, \tag{4.18}$$

and if the function $G_{l_1 l_2 L}(x)$, or, equivalently, the function $F_{l_1 l_2 L}(x)$, is the same for both gases. Equations (4.17) and (4.18) imply that the equation

$$I_{\mathrm{A}}\, m_{\mathrm{B}}\,(d^{\mathrm{B}}{}_{l_1 l_2 L})^2 = I_{\mathrm{B}}\, m_{\mathrm{A}}\,(d^{\mathrm{A}}{}_{l_1 l_2 L})^2 \tag{4.19}$$

has to be obeyed. If there exists a choice of values of the $d_{l_1 l_2 L}$ such that this is the case and if $F^{\mathrm{A}}{}_{l_1 l_2 L}(x) = F^{\mathrm{B}}{}_{l_1 l_2 L}(x)$ for this choice, then Eq. (4.16) may be written as

$$\begin{aligned} &\langle l_1 l_2 L |\, \sigma\binom{pqst}{p'q's't'}_k \,| l_1 l_2 L\rangle^{\mathrm{A}}(T) \\ &= \left\{\frac{I_{\mathrm{A}}\, C^{\mathrm{A}}{}_{l_1 l_2 L}\, d^{\mathrm{A}}{}_{l_1 l_2 L}}{I_{\mathrm{B}}\, C^{\mathrm{B}}{}_{l_1 l_2 L}\, d^{\mathrm{B}}{}_{l_1 l_2 L}}\right\}^2 \langle l_1 l_2 L |\, \sigma\binom{pqst}{p'q's't'}_k \,| l_1 l_2 L\rangle^{\mathrm{B}} . \\ &\cdot (I_{\mathrm{A}}\, T/I_{\mathrm{B}})\,. \end{aligned} \tag{4.20}$$

This is the sought-for law of corresponding states.

When the gases A and B are both homonuclear with atoms which are isotopes, then Eqs. (4.19) and (4.20) are certainly valid, since for two such molecules the relations

$$\begin{aligned} &d^{\mathrm{A}}{}_{l_1 l_2 L} = d^{\mathrm{B}}{}_{l_1 l_2 L}\,, \quad C^{\mathrm{A}}{}_{l_1 l_2 L} = C^{\mathrm{B}}{}_{l_1 l_2 L}\,, \\ &I_{\mathrm{A}}\, m_{\mathrm{B}} = I_{\mathrm{B}}\, m_{\mathrm{A}}\,, \end{aligned} \tag{4.21}$$

are very closely satisfied. Equation (4.20) simplifies in that case to

$$\begin{aligned} &\langle l_1 l_2 L |\, \sigma\binom{pqst}{p'q's't'}_k \,| l_1 l_2 L\rangle^{\mathrm{A}}(T) \\ &= (m_{\mathrm{A}}/m_{\mathrm{B}})^2 \langle l_1 l_2 L |\, \sigma\binom{pqst}{p'q's't'}_k \,| l_1 l_2 L\rangle^{\mathrm{B}}(m_{\mathrm{A}}\, T/m_{\mathrm{B}})\,. \end{aligned} \tag{4.22}$$

If the intermolecular potential is such that no cross terms between different types of potential have to be taken into account for the cross section under consideration, then Eq. (4.22) implies

$$\sigma\binom{pqst}{p'q's't'}_k{}^{\mathrm{A}}(T) = (m_{\mathrm{A}}/m_{\mathrm{B}})^2\, \sigma\binom{pqst}{p'q's't'}(m_{\mathrm{A}}\, T/m_{\mathrm{B}})\,. \tag{4.23}$$

This formula may be expected to be useful for, e.g., the prediction of the temperature dependence of a cross section for $^{15}\mathrm{N}_2$ from the (presumably) measured temperature dependence of the same cross section for $^{14}\mathrm{N}_2$. If the two isotopes have different $g(j)$ functions (e.g., H_2 and D_2), then Eq. (4.22) is not valid (at least not for low temperatures). In such a case the relation

$$I^{\mathrm{A}}{}_{l_1 l_2 L}(T) = (m_{\mathrm{A}}/m_{\mathrm{B}})^2\, I^{\mathrm{B}}{}_{l_1 l_2 L}(m_{\mathrm{A}}\, T/m_{\mathrm{B}}) \tag{4.24}$$

may still be useful. This is probably especially true for the hydrogen isotopes, for which the inelastic parts of $\sigma\binom{0k00}{0k00}^{(\prime)}$ are negligible.

5. Approximate Calculation of Multipole-Multipole Contributions

In the case of multipole-multipole interactions, the potential $\hat{V}_{l_1 l_2 L}(R)$ may be approximated using a model due to Chen and Snider [17]. This form is

$$\begin{aligned} &\hat{V}_{l_1 l_2 L}(R) = 0 && \text{if } R < d\,, \\ &\hat{V}_{l_1 l_2 L}(R) = V_{l_1 l_2 L}(R) = W_L\, R^{-L-1} && \text{if } R \geqq d\,. \end{aligned} \tag{5.1}$$

Here d is a hard-sphere diameter associated with the molecule, which in what follows will be inferred from the expression for $\sigma\binom{2000}{2000}$ for hard spheres [11]:

$$\sigma\binom{2000}{2000} = 4/5\, \pi\, d^2\,. \tag{5.2}$$

$\sigma\binom{2000}{2000}$ is related to the field-free shear viscosity coefficient η_0 (see Introduction) It should be noted that this choice of d makes $\hat{V}_{l_1 l_2 L}(R)$ temperature dependent; this feature of the approximation should improve the temperature dependence of the collision integrals evaluated with this model. On the other hand, the law of corresponding states derived in the previous section does not hold any longer, except for the isotope effect.

The quantity W_L occurring in Eq. (5.1) may be expressed in terms of the multipole moments of the molecules; in particular,

$$W_2 = 3\,\mu_e{}^2\,, \quad W_3 = (15/4)\,\mu_e\,Q_e\,, \quad W_4 = (105/4)\,Q_e{}^2, \tag{5.3}$$

where μ_e and Q_e are the scalar values of the molecular dipole and quadrupole moments, respectively.

With the use of Eq. (5.1), the quantity $C_{l_1 l_2 L}$ and the functions $F_{l_1 l_2 L}$ and $G_{l_1 l_2 L}$ may be calculated to be given by

$$C_{l_1 l_2 L} = W_L\,d^{-L-1}\,, \tag{5.4}$$

$$F_{l_1 l_2 L}(x) = \begin{cases} 0 & \text{if } x < 1\,, \\ x^{-L-1} & \text{if } x \geqq 1\,, \end{cases} \tag{5.5}$$

$$G_{l_1 l_2 L}(x) = j_{L-1}(x)/x\,. \tag{5.6}$$

With these equations, Eqs. (4.6-9) become

$$\begin{aligned}\sigma_{l_1 l_2 L}(\varepsilon) &= \exp(\varepsilon/2)\,I_{l_1 l_2 L}(|\varepsilon|) \\ &= \exp(\varepsilon/2)\,\sigma^{(0)}{}_{l_1 l_2 L}\,J_{l_1 l_2 L}(|\varepsilon|)\,,\end{aligned} \tag{5.7}$$

$$\begin{aligned}\sigma^{(0)}{}_{l_1 l_2 L} = \pi\, m\, W_L{}^2\, 2^{L+1}(L!)^2 \\ \times [\hbar^2 k\,T\,\mathrm{d}^{2L-2}(2\,L+1)!]^{-1}\,,\end{aligned} \tag{5.8}$$

$$\begin{aligned}J_{l_1 l_2 L}(|\varepsilon|) = \int_0^\infty \mathrm{d}y\, y^{-1}\{j_{L-1}(y)\}^2 \\ \times \exp\{-\beta^2 y^2 - \varepsilon^2/(16\,\beta^2 y^2)\}\,,\end{aligned} \tag{5.9}$$

$$\beta^2 = \hbar^2[4\,d^2\, m\,k\,T]^{-1}\,. \tag{5.10}$$

The integral (5.9) has to be calculated numerically (but see Appendix B for the special case that $\varepsilon = 0$). Once this is done, however, the contributions due to multipole-multipole interactions to the collision integrals of Section 2 may easily be calculated.

6. Summary

The theoretical results of the present article may be summarized as follows:

a) General exact (in the DWBA) expressions for a number of diagonal collision integrals have been derived in terms of a cross section $\sigma_{l_1 l_2 L}(\varepsilon)$ which may be calculated once $V_0(R)$ and $V_{l_1 l_2 L}(R)$ are known. These equations may be found in Section 2.

b) The aforementioned expressions have been reduced for a number of types of nonspherical potentials. From these, approximate expressions have been derived by means of the high temperature approximation. A number of approximate relations between different diagonal cross sections is also given. (Section 3 and Table II).

c) In Section 4 the Born approximation (with a suitably modified $\hat{V}_{l_1 l_2 L}(R)$ has been used to derive a relation between $\sigma\binom{0200}{2000}$ and $\sigma\binom{0010}{0010}$ for any type of nonspherical potential. Using the same approximation, a general (approximate) law of corresponding states is found.

d) A model for the transition operator for multipole-multipole interactions has been introduced in Section 5. This model reduces the calculation of collision integrals to one numerical integration for each value of the dimensionless energy transfer ε.

The expressions established in this article may be applied to a large number of problems. Before this can be done, however, much more experimental material has to be available. It would be particularly interesting to see the results of temperature studies of the shear viscosity Senftleben-Beenakker effects for a large number of gases.

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Appendix A

Evaluation of Traces over Degenerate Internal States

In order to evaluate traces over degenerate internal states the following procedure is used:

a) The trace is rewritten in the $\mathbf{r}^\wedge$ -representation by use of the relation

$$\begin{aligned}\langle \mathbf{r}^\wedge | \mathscr{P}_j [\boldsymbol{J}]^{(k)} \mathscr{P}_j | \mathbf{r}^{\wedge\prime} \rangle \\ = \alpha_j{}^{(k)}[\hat{\mathbf{r}}]^{(j)} \odot^j \mathbf{T}(j,k,j) \odot^j [\hat{\mathbf{r}}']^{(j)}\end{aligned} \tag{A.1}$$

with

$$\begin{aligned}\alpha_j{}^{(k)} = \frac{2^j(2\,j+1)!!\,(2\,j-1)!!}{4\,\pi(2\,j-k)!}\,i^k \\ \times \begin{cases}(1/2)^{k/2} & (k \text{ even}), \\ (1/2)^{(k+1)/2} & (k \text{ odd}).\end{cases}\end{aligned} \tag{A.2}$$

This equation may be inferred from a slightly different expression given in Reference 12.

In the case of Eq. (2.10) the result of this change of representation is:

$$\begin{aligned}\mathrm{tr}_{\mathrm{deg}}\{\mathscr{P}_j[\mathbf{r}^\wedge]^{(l)}\mathscr{P}_{j'}[\mathbf{r}^\wedge]^{(l)}\} \\ = \alpha_j{}^{(0)}\alpha_{j'}{}^{(0)} \iint \mathrm{d}\mathbf{r}^\wedge\,\mathrm{d}\mathbf{r}^{\wedge\prime}[\mathbf{r}^\wedge]^{(j)} \odot^j [\mathbf{r}^{\wedge\prime}]^{(j)} \\ \times [\mathbf{r}^{\wedge\prime}]^{(l)}[\mathbf{r}^{\wedge\prime}]^{(j')} \odot^{j'} [\mathbf{r}^\wedge]^{(j')}[\mathbf{r}^\wedge]^{(l)}\,.\end{aligned} \tag{A.3}$$

b) The integrals resulting after step a) are always of the form

$$\int \mathrm{d}\mathbf{r}^{\wedge}\,[\mathbf{r}^{\wedge}]^{(j)}\,[\mathbf{r}^{\wedge}]^{(k)}\,[\mathbf{r}^{\wedge}]^{(l)} = \mu(j,k,l)\,\mathbf{T}(j,k,l) \tag{A.4}$$

where [12]

$$\mu(j,k,l) = 4\pi \frac{j!\,k!\,l!}{(J+1)!!\,(\tfrac{1}{2}J-j)!\,(\tfrac{1}{2}J-k)!\,(\tfrac{1}{2}J-l)!} \tag{A.5}$$

if $J = j+k+l$ is even and if the of indices (j, k, l) satisfies the triangle inequalities. If one of these two conditions is not met, then $\mu(j, k, l) = 0$. This property gives rise to the collisional selection rules of Table I.

Equation (A.3) reduces to the following, when Eq. (A.4) is used:

$$\begin{aligned}&\mathrm{tr}_{\mathrm{deg}}\{\mathscr{P}_j\,[\mathbf{r}^{\wedge}]^{(l)}\,\mathscr{P}_{j'}[\mathbf{r}^{\wedge}]^{(l)}\}\\ &\qquad = \alpha_j{}^{(0)}\,\alpha_{j'}{}^{(0)}\,\mu^2(j,l,j')\,\mathbf{T}(\bar{j},l,\bar{j}')\,\mathbf{T}(\bar{j},l,\bar{j}'),\end{aligned} \tag{A.6}$$

where a bar over a digit in a $(3-j)$-tensor denotes a contraction of the corresponding set of indices. The result of this contraction may be found by contracting both sides of Eq. (A.6) completely:

$$\begin{aligned}&\mathrm{tr}_{\mathrm{deg}}\{\mathscr{P}_j\,[\mathbf{r}^{\wedge}]^{(l)} \odot^{l} \mathscr{P}_{j'}[\mathbf{r}^{\wedge}]^{(l)}\}\\ &\qquad = \alpha_j{}^{(0)}\,\alpha_{j'}{}^{(0)}\,\mu^2(j,l,j')\,\Omega(j,l,j'),\end{aligned} \tag{A.7}$$

where $\Omega(j,l,j') = T(\bar{j},\bar{l},\bar{j}')\,T(\bar{j},\bar{l},\bar{j}')$. The $\Omega(j,k,l)$ have been given by Coope[15] as

$$\Omega(j,k,l) = \frac{(J+1)!\,(J-2j)!\,(J-2k)!\,(J-2l)!}{(2j)!\,(2k)!\,(2l)!} \times \begin{cases} 1, & J = j+k+l \text{ even}, \\ 2, & J \text{ odd}. \end{cases} \tag{A.8}$$

A comparison of the contracted form of Eq. (2.10) and Eq. (A.7) shows now that $B_{jj'}^{(l)}$ is given by

$$B_{jj'}^{(l)} = \alpha_j{}^{(0)}\,\alpha_{j'}{}^{(0)}\,\mu^2(j,l,j')\,\Omega(j,l,j')\,(2l+1)^{-1}. \tag{A.9}$$

Tensorial contractions always constitute the last step c) in the evaluation of traces. In more complicated cases, these contractions may give rise to $(6-j)$-symbols, see References 12 and 15.

Appendix B

The Function $J_{l_1 l_2 L}(0)$

The function $J_{l_1 l_2 L}(|\varepsilon|)$ introduced in Eq. (5.9) may be evaluated analytically for energetically elastic collisions, the result being[18]

$$\begin{aligned}J_{l_1 l_2 L}(0) &= \int_0^\infty \mathrm{d}y\, y^{-1}\{j_{L-1}(y)\}^2 \exp[-\beta^2 y^2]\\ &= \frac{\pi(L-2)!}{2^{2L+1}\beta^{2L-2}\{\Gamma(L+\frac{1}{2})\}^2}\, {}_2F_2\left(\begin{matrix} L & L-1 \\ L+\frac{1}{2} & 2L \end{matrix}\middle| -\frac{1}{\beta^2}\right)\end{aligned} \tag{B.1}$$

where ${}_2F_2$ is a generalized hypergeometric function[18]. In many cases β is so small that it may be set equal to zero. In this special case the integral is of Weber-Schafheitlin type and has the value[18]

$$\begin{aligned}J_{l_1 l_2 L}(0)\,|^{\beta=0} &= \int_0^\infty \mathrm{d}y\, y^{-1}\{j_{L-1}(y)\}^2\\ &= [2L(L-1)]^{-1}.\end{aligned} \tag{B.2}$$

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