

# Transport properties of asymmetric-top molecules

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Kinetic theory of gases is extended from linear molecules to asymmetric tops. The integration over the velocity of the centre of mass is carried out explicitly and the results are expressed in a form suitable for classical evaluation. These results can also be employed for spherical and symmetric tops.

## 1. Introduction

Dilute-gas transport properties, such as the shear viscosity and the thermal conductivity, are of great interest, particularly as absolute values can be measured in favourable cases with an uncertainty less than  $\pm(0.1-0.2)\%$  and  $\pm(0.3-0.5)\%$ , respectively.<sup>1</sup> The kinetic theory of dilute gases allows the calculation of these and other transport and relaxation properties from a set of effective cross sections, known as Omega integrals for atomic gases. These cross sections can be determined from a given intermolecular potential energy hypersurface and the quality of the surface can be tested by comparison with measurements of the transport properties calculated employing it. Typically, the best measurements are made at room temperature but, depending on the molecule of interest, results may be available over a wide range of temperatures, albeit with varying accuracy. Kinetic theory can also be used to predict the transport properties at temperatures outside the working range of most instruments, especially at high temperatures.

The kinetic theory of dilute monatomic gases has been very successfully applied to calculate reference values for the transport properties of helium to be used for the calibration of measuring instruments. Prerequisites for such a calibration are that the kinetic theory for monatomic gases requires only minimal approximations to be implemented practically, and that a highly precise interatomic potential has been determined.<sup>2</sup>

For linear molecules Curtiss<sup>3</sup> has provided the necessary kinetic theory in a form amenable to numerical evaluation. Using this, calculations have been performed for nitrogen,<sup>4,5</sup> carbon monoxide,<sup>6,7</sup> and carbon dioxide.<sup>8-10</sup> These calculations were based on a classical description of the two-molecule scattering process with rigid monomers and resulted in the successful evaluation of a number of transport properties and of magnetic-field effects on these properties, as well as of relaxation properties. All three molecules are relatively rigid due to their double or triple bonds and have sufficiently large masses and moments of inertia that a classical description with rigid molecules is justified for most of the transport and

relaxation properties. However, in order to describe adequately the thermal conductivity and thermo-magnetic effects, vibrational modes of motion have had to be taken into account by a physically reasonable correction.<sup>9,11</sup> Since the thermomagnetic, viscomagnetic and relaxation properties vanish for a spherically symmetric potential, these properties are direct indicators of the anisotropy of the potential surfaces.

Extending kinetic theory to rigid molecules of arbitrary structure, asymmetric tops, and implementing it in a computer code using a similar classical rigid-molecule scattering description, is the next evolutionary step in this development. The present paper is concerned with deriving the necessary expressions. This development will allow the calculation, for the first time, of the transport and relaxation properties of molecules such as dilute gas-phase water, using different intermolecular potential hypersurfaces reported in the literature, *e.g.* ref. 12 and 13. Furthermore, since symmetric tops and spherical tops can be considered as special cases of asymmetric tops, this development will allow transport and relaxation properties of important molecules such as benzene, methane and sulfur hexafluoride to be calculated. However, molecules such as ethane and ammonia, which are not completely rigid, may still present additional problems, due to internal rotation for the former and “umbrella” inversion for the latter.

## 2. Theory

### 2.1 Boltzmann equation

Dilute gas transport theory is based on solving the linearised Boltzmann equation for the relevant perturbation.<sup>14</sup> The classical Boltzmann equation for linear molecules was derived by Curtiss<sup>15</sup> and later extended by him to non-reacting molecules of arbitrary structure.<sup>16</sup> However, while he provided a detailed description of the calculation of effective cross sections for linear molecules,<sup>3</sup> no such description is available for asymmetric tops.

For the classical coordinates for the asymmetric top of interest here we employ  $J$ ,  $K$ ,  $M$ ,  $q_J$ ,  $q_K$ ,  $q_M$ , where  $J$  is the magnitude of the angular momentum vector,  $\mathbf{J}$ , of the top,  $K$  and  $M$  are its projections on the body-fixed and space-fixed  $z$  axes, respectively, and  $q_J$ ,  $q_K$  and  $q_M$  are the corresponding conjugate angle variables. A useful figure illustrating these angles can be found in ref. 17 or in ref. 18. (Note that these coordinates for an asymmetric top are identical to those for a

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symmetric top.) For free motion of the top  $J$ ,  $M$  and  $q_M$  are constant. For the special case of a symmetric top,  $K$  is also constant and  $q_J$  and  $q_K$  increase linearly with time, while for a spherical top  $q_K$  is also constant.

We assume that for an asymmetric-top molecule the distribution function,  $f_a$ , depends on  $K$  and  $q_K$  only implicitly through the internal energy of the top, given by<sup>19,20</sup>

$$E_a(J, K, q_K) = J^2 \left( \frac{\cos^2 q_K}{2I_x^a} + \frac{\sin^2 q_K}{2I_y^a} \right) + K^2 \left( \frac{1}{2I_z^a} - \frac{\cos^2 q_K}{2I_x^a} - \frac{\sin^2 q_K}{2I_y^a} \right), \quad (2.1)$$

where  $I_x^a$ ,  $I_y^a$  and  $I_z^a$  are the principal moments of inertia ( $I_z^a \geq I_y^a \geq I_x^a$ ). Here we are following Liu *et al.*<sup>17</sup> and Yang *et al.*<sup>18</sup> in using the “y-convention” of Goldstein *et al.*<sup>21</sup> for the definition of the conventional Euler angles used to define the orientation of the top. This choice leads to the interchange of  $\sin q_K$  and  $\cos q_K$  in the expression of Augustin and Miller<sup>19</sup> for the energy of the top, our eqn (2.1). For a symmetric top we take  $I_x^a = I_y^a$ , regardless of the relative size of  $I_z^a$ .

Ideally, as well as this implicit dependence on  $K$  and  $q_K$ , an explicit dependence would also be introduced. This would complicate the development significantly, requiring two additional indices in the basis functions used to represent the distribution function. In turn, four additional indices would be required for the effective cross sections. Hence inclusion of this  $K$  and  $q_K$  dependence is deferred until there is clear experimental evidence that inclusion is required and we solve for the distribution function averaged over  $K$  and  $q_K$ . Such averaging is equivalent to taking the lowest term in a more general expansion of  $f_a$  which allows for the explicit dependence on  $K$  and  $q_K$ . However, the  $K$  dependence might be relevant for studying electric-field effects on transport properties, since, in general, the energy of an asymmetric top in an electric field depends on the value of  $K$ .

As for a linear molecule, we assume also that  $f_a$  is independent of  $q_J$  and of  $\mathbf{R}$ , the position of the molecule centre of mass.

The Boltzmann equation for the distribution function for an asymmetric top, species  $a$ , in collision with an asymmetric top, species  $b$ , is<sup>16</sup>

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + \frac{1}{m_a} \mathbf{P}^a \cdot \nabla_a \right) f_a(\mathbf{P}_a, E_a, \cos \theta_{M_a}, q_{M_a}) \\ &= \frac{1}{8\pi^2} \int (f'_a f'_b - f_a f_b) g b \, db \, d\phi_b \, d\mathbf{P}_b \, J_b^2 \, dJ_b \, d(\cos \theta_{K_b}) \\ & \times dq_{J_b} \, dq_{K_b} \, dq_{M_b} \, dq_{J_a} \, d(\cos \theta_{K_a}) \, dq_{K_a}, \end{aligned} \quad (2.2)$$

where  $m_a$  and  $\mathbf{P}_a$  are the molecular mass and momentum of species  $a$ , respectively and generally subscripts  $a$  and  $b$  denote properties of species  $a$  and  $b$ , respectively. Here  $\mathbf{g}$  and  $\mathbf{b}$  are the relative velocity and impact-parameter vectors, respectively,  $\phi_b$  is the azimuthal angle of  $\mathbf{b}$  about  $\mathbf{g}$ ,  $\cos \theta_{M_a} = M_a/J_a$  and the right-hand side has been averaged over the variables  $q_J$ ,  $K_a$  and  $q_{K_a}$ , extending the averaging over  $q_{J_a}$  used by Curtiss<sup>15</sup> for the linear-molecule case. For convenience, the average over  $K_a$

is replaced by an average over  $\theta_{K_a}$ , the angle between  $\mathbf{J}_a$  and the body-fixed  $z$  axis, and similarly for the integral over  $K_b$ . We assume no ambiguity results from the use of  $b$  to denote both the impact parameter and a species label.

The zero-order equilibrium solution for the distribution function is

$$f_a^{(0)}[P_a, E_a(J_a, K_a, q_{K_a}), T] = \frac{n_a}{(2\pi m_a k_B T)^{3/2} Z_a} \times \exp\left(-\frac{P_a^2}{2m_a k_B T} - \frac{E_a}{k_B T}\right), \quad (2.3)$$

where  $T$  is the temperature,  $n_a$  is the number of molecules of species  $a$ ,  $Z_a = (2\pi k_B T)^{3/2} (I_x^a I_y^a I_z^a)^{1/2}$  is proportional to the classical internal state partition function and  $k_B$  is Boltzmann's constant.

The normalization is

$$\int f_a^{(0)}[P_a, E_a(J, K, q_K), T] \, d\mathbf{P}_a \, dJ \, dM \, dq_M \, \frac{dK}{2} \, \frac{dq_K}{2\pi} = n_a. \quad (2.4)$$

To verify the normalization we note that

$$\begin{aligned} & \int_0^\infty dJ \int_{-J}^J dM \int_{-J}^J \frac{dK}{2} \int_0^{2\pi} \frac{dq_K}{2\pi} g[E_a(J, K, q_K)] \\ &= \frac{1}{\pi} \int_0^{2\pi} dq_K \int_0^\infty J dJ \int_0^J dK g(E_a) \\ &= \frac{1}{\pi} \int_0^{2\pi} dq_K \int_0^\infty dK \int_K^\infty J dJ g(E_a) \\ &= \frac{1}{\pi} \int_0^{2\pi} dq_K \int_0^\infty dK \int_{K^2/2I_z^a}^\infty \left( \frac{I_x^a I_y^a}{I_x^a \sin^2 q_K + I_y^a \cos^2 q_K} \right) g(E_a) dE_a \\ &= \frac{I_x^a I_y^a}{\pi} \int_0^{2\pi} \frac{dq_K}{I_x^a \sin^2 q_K + I_y^a \cos^2 q_K} \int_0^\infty g(E_a) dE_a \int_0^{\sqrt{2I_z^a E_a}} dK \\ &= \frac{8I_x^a I_y^a}{\pi} \int_0^{\pi/2} \frac{dq_K}{(I_x^a + I_y^a) + (I_y^a - I_x^a) \cos 2q_K} \int_0^\infty g(E_a) dE_a \sqrt{2I_z^a E_a} \\ &= 2(2I_x^a I_y^a I_z^a)^{1/2} \int_0^\infty \sqrt{E_a} g(E_a) dE_a, \end{aligned} \quad (2.5)$$

where  $g(E)$  is an arbitrary function of  $E$ .

## 2.2 Basis functions

The solution of the linearized Boltzmann equation is expressed in terms of suitable basis functions. We make minor modifications to the basis functions introduced for linear molecules in Curtiss.<sup>3</sup> We have introduced a phase change, multiplying by a factor of  $(i)^{p+q}$ ,  $i = \sqrt{-1}$ , to ensure all effective cross sections are real.<sup>4</sup> This choice gives the same phase convention as that employed by McCourt *et al.*<sup>14</sup> The second change involved alteration of one of the indices of the Associated Laguerre polynomial used for the internal energy arising from asymmetric tops requiring three generalized coordinates while the

linear molecules used previously required two.

$$\begin{aligned} \mathcal{B}_{km}^{pqst}(\mathbf{W}, \varepsilon, \hat{\mathbf{J}}) &= (-1)^{k-m} (i)^{p+q} 2\pi^{3/2} (2k+1)^{1/2} \\ &\times W^p \bar{L}_s^{p+1/2} (W^2) \varepsilon^{q/2} \bar{L}_t^{q+1/2}(\varepsilon) \\ &\times \sum_{\mu\nu} \begin{pmatrix} p & q & k \\ \mu & \nu & -m \end{pmatrix} Y_p^\mu(\hat{\mathbf{W}}) Y_q^\nu(\hat{\mathbf{J}}). \end{aligned} \quad (2.6)$$

The dimensionless linear momentum,  $\mathbf{W}_a$ , and rotational energy,  $\varepsilon_a$ , are given by

$$\mathbf{W}_a = \frac{\mathbf{P}_a}{(2m_a k_B T)^{1/2}}, \quad \varepsilon_a = \frac{E_a}{k_B T}, \quad (2.7)$$

where  $E_a$  is given by eqn (2.1). Here  $\bar{L}_n^m(x)$  is the normalised Associated Laguerre polynomial satisfying<sup>3</sup>

$$\int_0^\infty x^z \exp(-x) \bar{L}_n^z(x) \bar{L}_{n'}^z(x) dx = \delta_{n,n'}, \quad (2.8)$$

$\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$  denotes a 3-j symbol and  $Y_l^m(\hat{\mathbf{R}})$  denotes a spherical harmonic. Since we are following Curtiss,<sup>3</sup> eqn (2.6) uses the conventions of Hirschfelder *et al.*<sup>22</sup> for spherical harmonics.

The  $\mathcal{B}_{km}^{pqst}(\mathbf{W}, \varepsilon, \hat{\mathbf{J}})$  form an orthonormal set with weight function  $f_a^{(0)}$ :

$$\begin{aligned} &\frac{1}{n_a} \int f_a^{(0)} [P, E(J, K, q_K), T] \mathcal{B}_{k'l'm'}^{p'q's't'}(\mathbf{W}, \varepsilon, \hat{\mathbf{J}})^* \\ &\times \mathcal{B}_{km}^{pqst}(\mathbf{W}, \varepsilon, \hat{\mathbf{J}}) d\mathbf{P} dJ d\hat{\mathbf{J}} \frac{dK}{2} \frac{dq_K}{2\pi} = \delta(pqstkm|p'q's't'k'l'm'), \end{aligned} \quad (2.9)$$

where  $Z^*$  denotes the complex conjugate of  $Z$  and  $\delta(i_1 i_2 \cdots i_3 i_4 \cdots)$  is a shorthand for  $\delta_{i_1 i_3} \delta_{i_2 i_4} \cdots$ . Because  $\hat{\mathbf{J}}$  is independent of  $K$  and  $q_K$ , (see Child,<sup>20</sup> p. 87) or the figure in Liu *et al.*<sup>17</sup> or in Yang *et al.*<sup>18</sup>) the integration over  $\hat{\mathbf{J}}$  proceeds as for linear molecules. Also the integration over  $J, K, M$  and  $q_K$  proceeds as in eqn (2.5).

### 2.3 Effective cross sections

**2.3.1 Laboratory frame cross sections.** Using these basis functions from eqn (2.6) we then define, following Curtiss,<sup>3</sup> temperature-dependent effective cross sections in the laboratory reference frame, as

$$\begin{aligned} \sigma' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)} (T) &= -[64\pi^4 n_a n_b \bar{g}]^{-1} \\ &\times \frac{1}{2k+1} \sum_{m=-k}^k \int f_a^{(0)} f_b^{(0)} \mathcal{B}_{km}^{p'q's't'}(\mathbf{W}_a, \varepsilon_a, \hat{\mathbf{J}}_a)^* \\ &\times [\mathcal{B}_{km}^{pqst}(\mathbf{W}'_a, \varepsilon'_a, \hat{\mathbf{J}}'_a) - \mathcal{B}_{km}^{pqst}(\mathbf{W}_a, \varepsilon_a, \hat{\mathbf{J}}_a)] g b d b d \phi_b \\ &\times J_a^2 J_b^2 dJ_a dJ_b dR_a^{(0)} dR_b^{(0)} d\mathbf{P}_a d\mathbf{P}_b d\hat{\mathbf{r}}_{K_a} d\hat{\mathbf{r}}_{K_b}, \end{aligned} \quad (2.10)$$

and

$$\begin{aligned} \sigma'' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)} (T) &= -[64\pi^4 n_a n_b \bar{g}]^{-1} \\ &\times \frac{1}{2k+1} \sum_{m=-k}^k \int f_a^{(0)} f_b^{(0)} \mathcal{B}_{km}^{p'q's't'}(\mathbf{W}_b, \varepsilon_b, \hat{\mathbf{J}}_b)^* \\ &\times [\mathcal{B}_{km}^{pqst}(\mathbf{W}'_a, \varepsilon'_a, \hat{\mathbf{J}}'_a) - \mathcal{B}_{km}^{pqst}(\mathbf{W}_a, \varepsilon_a, \hat{\mathbf{J}}_a)] g b d b d \phi_b \\ &\times J_a^2 J_b^2 dJ_a dJ_b dR_a^{(0)} dR_b^{(0)} d\mathbf{P}_a d\mathbf{P}_b d\hat{\mathbf{r}}_{K_a} d\hat{\mathbf{r}}_{K_b}, \end{aligned} \quad (2.11)$$

where  $\bar{g}$  denotes the mean relative speed and

$$dR_\alpha^{(0)} = d\hat{\mathbf{J}}_\alpha d q_{J_\alpha}, \quad d\hat{\mathbf{r}}_{K_\alpha} = d(\cos \theta_{K_\alpha}) d q_{K_\alpha}, \quad \alpha \equiv a, b. \quad (2.12)$$

The overall normalization of these expressions for the cross sections is chosen so that if all the terms in  $\mathcal{B}$  are replaced by

$$P(b) = 1, \quad 0 \leq b \leq b_0, \quad P(b) = 0 \text{ elsewhere,}$$

then  $\sigma' = \sigma'' = \pi b_0^2$ . Equivalently, the cross section can be defined, analogously to quantal effective cross sections, in terms of the classical cross section differential in solid angle and in final rotor action variables.

We recall that Curtiss<sup>3</sup> uses primes for *pre-collision* values and, in Curtiss and Tonsager,<sup>23</sup> regards initial values as functions of final values. The classical trajectory (CT) linear-molecule code<sup>24</sup> reverses this convention. As in that paper, we shall use primes to denote post-collision values and regard final dynamical variables as functions of their pre-collision values. Note that, because of the absence of a preferred direction in space, each term in the sum in eqns (2.10) and (2.11) is independent of  $m$ .

We have used the notation

$$\sigma' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)} (T)$$

and

$$\sigma'' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)} (T)$$

to keep as close to Curtiss<sup>3</sup> as possible and to keep the notation as compact as possible. In terms of the notation used by McCourt *et al.* (see ref.14, section 2.3.2 and 5.2).

$$\begin{aligned} \sigma' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)} (T) &\cong \begin{pmatrix} p & q & s & t & | & a \\ p' & q' & s' & t' & | & a \end{pmatrix}_{ab}, \\ \sigma'' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)} (T) &\cong \begin{pmatrix} p & q & s & t & | & a \\ p' & q' & s' & t' & | & b \end{pmatrix}_{ab}. \end{aligned}$$

Thus, following McCourt *et al.*,<sup>14</sup> (see section 2.3.2)  $\sigma'$  accounts for the production of  $\mathcal{B}_{km}^{pqst}(\mathbf{W}, \varepsilon, \hat{\mathbf{J}})$  in species  $a$  from  $\mathcal{B}_{km}^{p'q's't'}(\mathbf{W}, \varepsilon, \hat{\mathbf{J}})$  in species  $a$  by collisions between species  $a$  and  $b$ , while  $\sigma''$  accounts for the production of  $\mathcal{B}_{km}^{pqst}(\mathbf{W}, \varepsilon, \hat{\mathbf{J}})$  in species  $a$  from  $\mathcal{B}_{km}^{p'q's't'}(\mathbf{W}, \varepsilon, \hat{\mathbf{J}})$  in species  $b$  by collisions

between the two species. This distinction between the primed and double-primed quantities is maintained throughout the paper.

For a full discussion of a gas mixture one would need a  $\sigma'$  cross section for the production of  $\mathcal{B}_{km}^{pqst}(\mathbf{W}, \varepsilon, \hat{\mathbf{J}})$  in species  $b$  from  $\mathcal{B}_{km}^{p'q's't'}(\mathbf{W}, \varepsilon, \hat{\mathbf{J}})$  in species  $a$  by collisions between species  $a$  and  $b$ . The derivation of this will mirror that for the species  $a$  case discussed here.

Substituting in eqns (2.10) and (2.11) for the equilibrium distribution functions from eqn (2.3) we obtain

$$\begin{aligned} \sigma' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)}(T) &= -[2^9 \pi^7 (k_B T)^3 (m_a m_b)^{3/2} Z_a Z_b \bar{g}]^{-1} \\ &\times \frac{1}{2k+1} \sum_{m=-k}^k \int \exp[-(W_a^2 + W_b^2 + \varepsilon_a + \varepsilon_b)] \\ &\times \mathcal{B}_{km}^{p'q's't'}(\mathbf{W}_a, \varepsilon_a, \hat{\mathbf{J}}_a)^* [\mathcal{B}_{km}^{pqst}(\mathbf{W}'_a, \varepsilon'_a, \hat{\mathbf{J}}'_a) - \mathcal{B}_{km}^{pqst}(\mathbf{W}_a, \varepsilon_a, \hat{\mathbf{J}}_a)] \\ &\times gb db d\phi_b J_a^2 J_b^2 dJ_a dJ_b dR_a^{(0)} dR_b^{(0)} d\mathbf{P}_a d\mathbf{P}_b d\hat{\mathbf{r}}_{K_a} d\hat{\mathbf{r}}_{K_b}, \end{aligned} \quad (2.13)$$

and with a similar expression for  $\sigma'' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)}(T)$ .

Again following Curtiss,<sup>3</sup> since the dynamics of the collision are independent of the velocity of the centre of mass, we transform from  $\mathbf{P}_a$  and  $\mathbf{P}_b$  to the relative velocity,  $\mathbf{g}$ , and the centre-of-mass velocity,  $\mathbf{G}$ , yielding:

$$\begin{aligned} \sigma' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)}(T) &= -[2^9 \pi^7 (k_B T)^3 Z_a Z_b \bar{g}]^{-1} \frac{(m_a m_b)^{3/2}}{2k+1} \\ &\times \sum_{m=-k}^k \int \exp \left[ -\left( \frac{MG^2}{2k_B T} + \frac{\mu g^2}{2k_B T} + \varepsilon_a + \varepsilon_b \right) \right] \\ &\times \mathcal{B}_{km}^{p'q's't'}(\mathbf{W}_a, \varepsilon_a, \hat{\mathbf{J}}_a)^* [\mathcal{B}_{km}^{pqst}(\mathbf{W}'_a, \varepsilon'_a, \hat{\mathbf{J}}'_a) - \mathcal{B}_{km}^{pqst}(\mathbf{W}_a, \varepsilon_a, \hat{\mathbf{J}}_a)] \\ &\times gb db d\phi_b J_a^2 J_b^2 dJ_a dJ_b dR_a^{(0)} dR_b^{(0)} d\mathbf{G} d\mathbf{g} d\hat{\mathbf{r}}_{K_a} d\hat{\mathbf{r}}_{K_b}, \end{aligned} \quad (2.14)$$

where  $M = m_a + m_b$ ,  $\mu$  denotes the reduced mass and a similar expression exists for

$$\sigma'' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)}(T).$$

**2.3.2 Integration over the centre of mass velocity.** Now, following Curtiss,<sup>3</sup> eqn (22), we transform the translational part of the integrand to centre-of-mass and relative coordinates. Fortunately, this proceeds exactly as for linear molecules since the internal structure of the molecules is not

involved. For asymmetric-top molecules we have

$$\begin{aligned} &\left( \frac{M}{2k_B T} \right)^{3/2} \frac{1}{2k+1} \sum_{m=-k}^k \iiint d\mathbf{G} \exp \left[ -\frac{MG^2}{2k_B T} \right] \\ &\times \mathcal{B}_{km}^{p'q's't'}(\mathbf{W}_a, \varepsilon_a, \hat{\mathbf{J}}_a)^* [\mathcal{B}_{km}^{pqst}(\mathbf{W}'_a, \varepsilon'_a, \hat{\mathbf{J}}'_a) - \mathcal{B}_{km}^{pqst}(\mathbf{W}_a, \varepsilon_a, \hat{\mathbf{J}}_a)] \\ &= \left( \frac{4\pi^3}{2^3 \pi^{5/2}} \right) (-1)^{k+p'} (-i)^{q+q'} \frac{\pi^2}{2} \\ &\times (2q+1)^{1/2} \varepsilon_a^{(q+q')/2} \sum_{\kappa} (-1)^{\kappa} (2\kappa+1) \begin{Bmatrix} q & q' & \kappa \\ p' & p & k \end{Bmatrix} \\ &\times \sum_{nl'l'} i^{l-l'} (2l+1)^{1/2} I_{nl'l'}^{(\kappa)}(y_a, y_b) \gamma^{l'} \bar{L}_n^{l'+1/2}(\gamma^2) \bar{L}_t^{q'+1/2}(\varepsilon_a) \\ &\times [(\gamma')^l \bar{L}_n^{l+1/2}(\gamma'^2) \bar{L}_t^{q+1/2}(\varepsilon'_a) X'(lq|l'q')_{\kappa} \\ &- \gamma^l \bar{L}_n^{l+1/2}(\gamma^2) \bar{L}_t^{q+1/2}(\varepsilon_a) X'(lq|l'q')_{\kappa}^{(0)}], \end{aligned} \quad (2.15)$$

where

$$\begin{Bmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{Bmatrix}$$

denotes a 6-j symbol,  $I_{nl'l'}^{(\kappa)}(y_a, y_b)$  denotes the Talmi coefficient used by Curtiss,<sup>3</sup> eqn (27),  $y_{\alpha}^2 = m_{\alpha}/M$ ,  $\alpha = a, b$ ,  $X'$  is as defined by Curtiss,<sup>3</sup> eqn (28), and where in  $X'(lq|l'q')_{\kappa}^{(0)}$  all primed dynamical variables are replaced by their unprimed equivalents. (Note that the indices  $nl'l'$  of  $I^{(\kappa)}$  have been transposed in Curtiss's eqns (30), (36–37) and (40–41).<sup>25</sup>) In eqn (2.15) the first term in parentheses on the right-hand side is the additional factor arising from the change in the numerical factors in the basis functions between linear molecules and asymmetric-top molecules. Similarly

$$\begin{aligned} &\left( \frac{M}{2k_B T} \right)^{3/2} \frac{1}{2k+1} \sum_{m=-k}^k \iiint d\mathbf{G} \exp \left[ -\frac{MG^2}{2k_B T} \right] \\ &\times \mathcal{B}_{km}^{p'q's't'}(\mathbf{W}_b, \varepsilon_b, \hat{\mathbf{J}}_b)^* [\mathcal{B}_{km}^{p'q's't'}(\mathbf{W}_a, \varepsilon_a, \hat{\mathbf{J}}_a) - \mathcal{B}_{km}^{pqst}(\mathbf{W}'_a, \varepsilon'_a, \hat{\mathbf{J}}'_a)] \\ &= (-1)^{k+p'} (-i)^{q+q'} \times \frac{\pi^{5/2}}{4} (2q+1)^{1/2} \varepsilon_a^{q/2} \varepsilon_b^{q'/2} \sum_{\kappa} (-1)^{\kappa} (2\kappa+1) \\ &\times \begin{Bmatrix} q & q' & \kappa \\ p' & p & k \end{Bmatrix} \sum_{nl'l'} i^{l+l'} \left( \frac{y_a}{y_b} \right)^{(4n'+2l'-2s'-p')} \\ &\times (2l+1)^{1/2} I_{nl'l'}^{(\kappa)}(y_a, y_b) \gamma^{l'} \bar{L}_n^{l'+1/2}(\gamma^2) \bar{L}_t^{q'+1/2}(\varepsilon_b) \\ &\times [(\gamma')^l \bar{L}_n^{l+1/2}(\gamma'^2) \bar{L}_t^{q+1/2}(\varepsilon'_a) X''(lq|l'q')_{\kappa} \\ &- \gamma^l \bar{L}_n^{l+1/2}(\gamma^2) \bar{L}_t^{q+1/2}(\varepsilon_a) X''(lq|l'q')_{\kappa}^{(0)}], \end{aligned} \quad (2.16)$$

and  $X''$  is defined by Curtiss,<sup>3</sup> eqn (29), and where in  $X''(lq|l'q')_{\kappa}^{(0)}$  all primed dynamical variables are replaced by their unprimed equivalents and where the scaled relative velocity

$$\boldsymbol{\gamma} = \left( \frac{\mu}{2k_B T} \right)^{1/2} \mathbf{g}, \quad (2.17)$$

has been introduced. Changing from integration over  $J_a$  and  $J_b$  to  $\varepsilon_a$  and  $\varepsilon_b$ , respectively, and employing eqn (30) from Curtiss,<sup>3</sup> for asymmetric-top molecules we have, where the change of variables proceeds as in eqn (2.5),

$$\begin{aligned} \sigma' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)} (T) &= -[2^{11}\pi^7]^{-1}(-1)^{k+p'}(-i)^{q+q'} \\ &\times \int \exp[-\gamma^2 - \varepsilon_a - \varepsilon_b] \gamma^3 (\varepsilon_a \varepsilon_b)^{1/2} (2q+1)^{1/2} \varepsilon_a^{(q+q')/2} \\ &\times \sum_{\kappa} (-1)^{\kappa} (2\kappa+1) \left\{ \begin{matrix} q & q' & \kappa \\ p' & p & k \end{matrix} \right\} \sum_{nl'l'} i^{l-l'} (2l+1)^{1/2} \\ &\times I_{ln'l';psp's'}^{(\kappa)}(y_a, y_b) \gamma^{l'} \bar{L}_{n'}^{l'+1/2}(\gamma^2) \bar{L}_{l'}^{q'+1/2}(\varepsilon_a) \\ &\times \left[ \begin{matrix} (\gamma')^l \bar{L}_n^{l+1/2}(\gamma'^2) \bar{L}_l^{q+1/2}(\varepsilon'_a) X'(lq|l'q')_{\kappa} \\ -\gamma^l \bar{L}_n^{l+1/2}(\gamma^2) \bar{L}_l^{q+1/2}(\varepsilon_a) X'(lq|l'q')_{\kappa}^{(0)} \end{matrix} \right] h(q_{K_a}; I_x^a, I_y^a) \\ &\times h(q_{K_b}; I_x^b, I_y^b) b db d\phi_b d\gamma d\hat{g} d\varepsilon_a d\varepsilon_b dR_a^{(0)} dR_b^{(0)} d\hat{r}_{K_a} d\hat{r}_{K_b}, \end{aligned} \quad (2.18)$$

where

$$\begin{aligned} h(q; I_x, I_y) &= \frac{\sqrt{I_x I_y}}{I_x \sin^2 q + I_y \cos^2 q}, \quad K_x = \sqrt{2\varepsilon_a k_B T I_z^2} \cos \bar{\theta}_{K_x}, \\ d\hat{r}_{K_a} &= d(\cos \bar{\theta}_{K_x}) dq_{K_x}, \quad \alpha \equiv a, b. \end{aligned} \quad (2.19)$$

Here  $d\hat{r}_{K_x}$  has been redefined from eqn (2.12) and no longer has the geometric interpretation introduced there. Note that for spherical and symmetric tops  $h = 1$  and that for asymmetric tops  $\bar{h} = \frac{2}{\pi} \int_0^{\pi/2} h dq = 1$ .

Alternatively, if the geometric interpretation in eqn (2.12) is to be retained, the factor  $(\varepsilon_a \varepsilon_b)^{1/2} h(q_{K_a}) h(q_{K_b})$  has to be replaced by

$$\frac{J_a J_b}{2k_B T \sqrt{I_z^a I_z^b}} \tilde{h}(\hat{r}_{K_a}; I_x^a, I_y^a, I_z^a) \tilde{h}(\hat{r}_{K_b}; I_x^b, I_y^b, I_z^b), \quad (2.20)$$

where

$$\tilde{h}(\hat{r}_K; I_x, I_y, I_z) = \frac{I_z \sqrt{I_x I_y}}{I_x \sin^2 q_K + I_y \cos^2 q_K} \sin^2 \theta_K + I_x I_y \cos^2 \theta_K. \quad (2.21)$$

For a spherical top  $\tilde{h} = 1$  and for a symmetric top  $\tilde{h}$  is independent of  $q_K$ .

Similarly

$$\begin{aligned} \sigma'' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)} (T) &= -[2^{11}\pi^7]^{-1}(-1)^{k+p'}(-i)^{q+q'} \\ &\times \int \exp[-\gamma^2 - \varepsilon_a - \varepsilon_b] \gamma^3 (\varepsilon_a \varepsilon_b)^{1/2} (2q+1)^{1/2} \varepsilon_a^{q/2} \varepsilon_b^{q'/2} \\ &\times \sum_{\kappa} (-1)^{\kappa} (2\kappa+1) \left\{ \begin{matrix} q & q' & \kappa \\ p' & p & k \end{matrix} \right\} \sum_{nl'l'} i^{l+l'} \left( \frac{y_a}{y_b} \right)^{(4n'+2l'-2s'-p')} \\ &\times (2l+1)^{1/2} I_{ln'l';psp's'}^{(\kappa)}(y_a, y_b) \gamma^{l'} \bar{L}_{n'}^{l'+1/2}(\gamma^2) \bar{L}_{l'}^{q'+1/2}(\varepsilon_b) \\ &\times [(\gamma')^l \bar{L}_n^{l+1/2}(\gamma'^2) \bar{L}_l^{q+1/2}(\varepsilon'_a) X''(lq|l'q')_{\kappa} \\ &- \gamma^l \bar{L}_n^{l+1/2}(\gamma^2) \bar{L}_l^{q+1/2}(\varepsilon_a) X''(lq|l'q')_{\kappa}^{(0)}] \\ &\times h(q_{K_a}; I_x^a, I_y^a) h(q_{K_b}; I_x^b, I_y^b) b db d\phi_b d\gamma d\hat{g} \\ &\times d\varepsilon_a d\varepsilon_b dR_a^{(0)} dR_b^{(0)} d\hat{r}_{K_a} d\hat{r}_{K_b}. \end{aligned} \quad (2.22)$$

Since only *relative* orientations are important we are free to choose our space-fixed axes with  $Oz$  along  $\mathbf{g}$  and  $Ox$  along  $\mathbf{b}$ . Then the integrand is independent of  $\phi_b$  and  $\hat{g}$  so performing the integral over these variables yields a factor of  $8\pi^2$ .

**2.3.3 Centre of mass cross sections.** Following Curtiss,<sup>3</sup> for asymmetric-top molecules we define angle averages of the integrands:

$$\begin{aligned} R' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_{\kappa} &= \frac{\varepsilon_a^{q/2}}{2^{10}\pi^6} \int (\gamma')^l \bar{L}_n^{l+1/2}(\gamma'^2) \\ &\times \bar{L}_l^{q+1/2}(\varepsilon'_a) X'(lq|l'q')_{\kappa} h(q_{K_a}; I_x^a, I_y^a) h(q_{K_b}; I_x^b, I_y^b) \\ &\times dR_a^{(0)} dR_b^{(0)} d\hat{r}_{K_a} d\hat{r}_{K_b}. \end{aligned} \quad (2.23)$$

Similarly, following Curtiss,<sup>3</sup> eqn (32), we define

$$R'' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_{\kappa}$$

as in eqn (2.23) but with  $X'(lq|l'q')_{\kappa}$  replaced by  $X''(lq|l'q')_{\kappa}$ .

We now define an energy-dependent cross section in the centre-of-mass frame:

$$\begin{aligned} Q' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_{\kappa} (\varepsilon_a, \varepsilon_b, \gamma) &= 2\pi \int_0^{\infty} b db \\ &\times \left[ \delta_{l,l'} \delta_{q,q'} \delta_{n,n'} \delta_{t,t'} \bar{L}_n^{l+1/2}(\gamma^2) \varepsilon_a^{q/2} \bar{L}_l^{q+1/2}(\varepsilon_a) - R' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_{\kappa} \right]. \end{aligned} \quad (2.24)$$

In the analogous cross section,

$$Q'' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_{\kappa} (\varepsilon_a, \varepsilon_b, \gamma),$$

in the first term inside the square brackets there is an additional factor of  $\delta_{q,0}$  and the second term is replaced by

$$R'' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_\kappa.$$

Next, we introduce the thermally averaged centre-of-mass cross sections:

$$\begin{aligned} \sigma' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_\kappa (T) &= i^{q-q'+l-l'} \int \exp[-\gamma^2 - \varepsilon_a - \varepsilon_b] \\ &\times (\varepsilon_a \varepsilon_b)^{1/2} \gamma^{l'} \bar{L}_{n'}^{l'+1/2}(\gamma^2) \bar{L}_{l'}^{q'+1/2}(\varepsilon_a) (\varepsilon_a)^{q'/2} \\ &\times Q' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_\kappa (\varepsilon_a, \varepsilon_b, \gamma) \gamma^2 d(\gamma^2) d\varepsilon_a d\varepsilon_b, \end{aligned} \quad (2.25)$$

and

$$\begin{aligned} \sigma'' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_\kappa (T) &= i^{q-q'+l-l'} \int \exp[-\gamma^2 - \varepsilon_a - \varepsilon_b] \\ &\times (\varepsilon_a \varepsilon_b)^{1/2} \gamma^{l'} \bar{L}_{n'}^{l'+1/2}(\gamma^2) \bar{L}_{l'}^{q'+1/2}(\varepsilon_b) (\varepsilon_b)^{q'/2} \\ &\times Q'' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_\kappa (\varepsilon_a, \varepsilon_b, \gamma) \gamma^2 d(\gamma^2) d\varepsilon_a d\varepsilon_b. \end{aligned} \quad (2.26)$$

The introduction of the leading factor in  $i$  on the right-hand side ensures that  $\sigma'$  and  $\sigma''$  are always real because  $X'(lq|l'q')_k$  is real or imaginary as  $(q - q' + l - l')$  is even or odd, respectively.

Finally we can relate the lab and centre-of-mass temperature-dependent cross sections. We have, from eqns (2.18) and (2.25),

$$\begin{aligned} \sigma' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)} (T) &= (-1)^{k+q+p'} (2q+1)^{1/2} \\ &\times \sum_\kappa (-1)^\kappa (2\kappa+1) \left\{ \begin{matrix} q & q' & \kappa \\ p' & p & k \end{matrix} \right\} \\ &\times \sum_{nl'l'} (2l+1)^{1/2} I_{nl'l'n';psp's'}^{(\kappa)}(y_a, y_b) \sigma' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_\kappa (T), \end{aligned} \quad (2.27)$$

with, for

$$\sigma'' \begin{pmatrix} p & q & s & t \\ p' & q' & s' & t' \end{pmatrix}^{(k)} (T),$$

an additional factor of  $(-1)^l (y_a/y_b)^{(4n'+2l-2s'-p')}$  inside the second summation and

$$\sigma' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_\kappa (T)$$

replaced by

$$\sigma'' \begin{pmatrix} l & q & n & t \\ l' & q' & n' & t' \end{pmatrix}_\kappa (T).$$

Hence we now have the necessary relations to determine the effective cross sections employed in kinetic theory from the detailed dynamical treatment of the collisions. Practical details concerning the implementation are discussed in the Appendix.

## 2.4 Semiclassical aspects

While this description is entirely classical, we note here some connections with semiclassical aspects for symmetric and asymmetric tops. For the symmetric top  $K$  is a good quantum number. Hence the methods used by Liu and Dickinson<sup>26</sup> can be employed to establish the connection between classical effective cross sections and quantal cross sections approximated using the classical S-matrix theory.<sup>27,28</sup>

For asymmetric tops, however,  $K$  is not a constant of the motion and transitions are described in the classical S-matrix theory by Augustin and Miller<sup>19</sup> in terms of the angular-momentum-like variable  $\eta$  where, in our notation,

$$\begin{aligned} \eta^2 &= (1+\kappa)K^2 - (1-\kappa)(J^2 - K^2) \cos^2 q_K, \\ \kappa &= \frac{2I_x I_z - I_y(I_x + I_z)}{I_y(I_z - I_x)}. \end{aligned} \quad (2.28)$$

Here  $\kappa$  denotes the usual asymmetry parameter for asymmetric tops, rather than the tensor rank index introduced in eqn (2.15). Thus for a semiclassical description<sup>19</sup> the natural variables are  $J, M, \eta, q_J, q_M, q_\eta$  and transition amplitudes are calculated assuming a uniform distribution in  $q_\eta$ , the angle variable conjugate to  $\eta$ . Effective cross sections involve sums over the quantized values of  $\eta$  and, in a semiclassical approximation, these sums are converted to integrals over  $\eta$ . Since the transformation between the canonical pairs  $(\eta, q_\eta)$  and  $(K, q_K)$  has Jacobian one, the resulting expressions can equally be evaluated in the  $K, q_K$  representation, as employed in our fully classical description.

A further issue concerns quantal effects in the energies of the asymmetric top. The quantization of the  $\eta$  variable involves motion in a symmetric double-well potential, qualitatively similar to that giving the inversion splitting in ammonia. Colwell *et al.*<sup>29</sup> have shown that a uniform semiclassical approximation, including allowance for tunnelling, gives much improved results over the standard WKB approximation ignoring tunnelling. As tunnelling leads to a splitting of otherwise degenerate levels and, for low tunnelling frequencies this splitting is approximately symmetric about the degenerate level, the overall effect can be expected to be quite small when a thermal average is required. Clearly this effect can be expected to be strongest for hydrides.

## 3. Summary and conclusions

Previously, only for linear molecules<sup>3</sup> was the necessary kinetic theory available for the calculation of transport and relaxation properties. Here we have extended this work to the most general rigid molecular structure, the asymmetric top. For the effective cross sections required by this theory we have performed the integration over the velocity of the centre of mass and brought the cross sections to a form suitable for classical trajectory calculation. The solution for asymmetric

tops necessarily includes the results for spherical and symmetric tops as special cases.

Calculations are in progress for methane and for water and will be reported separately.<sup>30</sup>

While the theory developed here has been focussed on pure gases, much of the development can readily be extended to mixtures. In particular, the integration over the centre of mass velocity has been performed for an arbitrary mass ratio of the colliding partners (see section 2.3.2).

## Appendix

### 3.1 Practical implementation

To follow as closely as possible the method used in the current linear-molecule code<sup>24</sup> we transform the centre of mass thermal average, eqn (2.25), to obtain just one temperature-dependent integral over the (conserved) total energy, translational and rotational. The procedure is outlined for  $\sigma'$ : a similar procedure may readily be adopted for  $\sigma''$ . The integral appearing in eqn (2.25) is of the form

$$\mathcal{J} = \int_0^\infty \int_0^\infty \int_0^\infty \exp[-\gamma^2 - \varepsilon_a - \varepsilon_b] \gamma^2 (\varepsilon_a \varepsilon_b)^{1/2} d(\gamma^2) d\varepsilon_a d\varepsilon_b \mathcal{F}. \quad (3.29)$$

Introducing new variables

$$\mathcal{E} = E/k_B T = \gamma^2 + \varepsilon_a + \varepsilon_b, \quad x = \gamma^2/\mathcal{E} = \mu g^2/2E, \quad (3.30)$$

$$y = \varepsilon_a/[(1-x)\mathcal{E}] = E_a/[(1-x)E],$$

where  $E$  is the total energy, eqn (3.29) becomes

$$\mathcal{J} = \int_0^\infty \mathcal{E}^4 \exp(-\mathcal{E}) d\mathcal{E} \int_0^1 x(1-x)^2 dx \times \int_0^1 \sqrt{y(1-y)} dy \mathcal{F}. \quad (3.31)$$

With a view to obtaining a more uniform integrand for the Monte Carlo numerical integration we make further transformations

$$u = 6x^2 - 8x^3 + 3x^4, \quad v = \frac{2}{\pi} \left( \alpha - \frac{1}{4} \sin 4\alpha \right), \\ y = \sin^2 \alpha, \quad \text{or} \quad v = \frac{2}{\pi} \left[ \arcsin \sqrt{y} - (1-2y)\sqrt{y(1-y)} \right], \quad (3.32)$$

yielding

$$\mathcal{J} = \frac{\pi}{96} \int_0^\infty \mathcal{E}^4 \exp(-\mathcal{E}) d\mathcal{E} \int_0^1 du \int_0^1 dv \mathcal{F}. \quad (3.33)$$

While we now have to solve eqn (3.32) numerically for  $x(u)$  and  $y(v)$  this is a trivial overhead. Introducing the transformed variables into eqn (2.25), the thermally averaged centre-of-mass cross section can be written

$$\sigma' \left( \begin{matrix} l & q & n & t \\ l' & q' & n' & t' \end{matrix} \right)_\kappa (T) = i^{q-q'+t-t'} \\ \times \frac{\pi}{96} \int_0^\infty \mathcal{E}^4 \exp(-\mathcal{E}) d\mathcal{E} \int_0^1 du \int_0^1 dv \mathcal{F}, \quad (3.34)$$

where

$$\mathcal{F} = \gamma^{l'} \bar{L}_{n'}^{l'+1/2}(\gamma^2) \bar{L}_{t'}^{q'+1/2}(\varepsilon_a) (\varepsilon_a)^{q'/2} \\ \times \mathcal{Q}' \left( \begin{matrix} l & q & n & t \\ l' & q' & n' & t' \end{matrix} \right)_\kappa (\varepsilon_a, \varepsilon_b, \gamma). \quad (3.35)$$

While we have written this thermal average in a form with just one explicitly temperature-dependent integral, that over  $\mathcal{E}$ , there remains an implicit temperature dependence through the variables  $\gamma$ ,  $\varepsilon_a$  and  $\varepsilon_b$ , particularly where they appear in the associated Laguerre polynomials. Following Curtiss and Tongsager,<sup>23</sup> we circumvent this problem by expanding the polynomials and dealing with simple powers of  $\gamma^2$ ,  $\varepsilon_a$  and  $\varepsilon_b$ , where we can use  $\gamma^2 = x\mathcal{E}$ , etc. from eqn (3.30) and thus separate the  $\mathcal{E}$  dependence. We write

$$\bar{L}_n^{l+1/2}(x) = \sum_{i=0}^n L(n, l, i) (-x)^i; \quad (3.36) \\ L(n, l, i) = \frac{\sqrt{\Gamma(n+1)\Gamma(n+l+3/2)}}{\Gamma(n-i+1)\Gamma(l+i+3/2)\Gamma(i+1)}.$$

To facilitate this transformation we introduce, following eqn (2.23),

$$R' \left( \begin{matrix} l & q & n & t \\ l' & q' & n' & t' \end{matrix} \right)_\kappa^{(0)} = \frac{\varepsilon_a^{q/2}}{2^{10}\pi^6} \int (\gamma)^l \bar{L}_n^{l+1/2}(\gamma^2) \\ \times \bar{L}_t^{q+1/2}(\varepsilon_a) X'(lq|l'q')_\kappa^{(0)} \\ \times h(q_{K_a}; I_x^a, I_y^a) h(q_{K_b}; I_x^b, I_y^b) dR_a^{(0)} dR_b^{(0)} d\hat{r}_{K_a} d\hat{r}_{K_b}, \\ = (\gamma)^l \bar{L}_n^{l+1/2}(\gamma^2) \varepsilon_a^{q/2} \bar{L}_t^{q+1/2}(\varepsilon_a) \delta_{l,l'} \delta_{q,q'} \delta_{\kappa,0}. \quad (3.37)$$

Now we can rewrite eqn (2.24)

$$\mathcal{Q}' \left( \begin{matrix} l & q & n & t \\ l' & q' & n' & t' \end{matrix} \right)_\kappa (\varepsilon_a, \gamma) = 2\pi \int_0^\infty b db \\ \times \left[ \delta_{l,l'} \delta_{q,q'} \delta_{\kappa,0} R' \left( \begin{matrix} l & q & n & t \\ l' & q' & n' & t' \end{matrix} \right)_\kappa^{(0)} - R' \left( \begin{matrix} l & q & n & t \\ l' & q' & n' & t' \end{matrix} \right)_\kappa \right]. \quad (3.38)$$

Substituting in the thermally-averaged cross section we can rewrite eqn (2.25)

$$\sigma' \left( \begin{matrix} l & q & n & t \\ l' & q' & n' & t' \end{matrix} \right)_\kappa (T) \\ = \sum_{i_1=0}^n \sum_{i_2=0}^t \sum_{i_3=0}^{n'} \sum_{i_4=0}^{t'} \sigma' \left( \begin{matrix} l & q & n & t & i_1 & i_2 \\ l' & q' & n' & t' & i_3 & i_4 \end{matrix} \right)_\kappa (T), \quad (3.39)$$

where

$$\begin{aligned} \bar{\sigma}' & \left( \begin{array}{cccccc} l & q & n & t & i_1 & i_2 \\ l' & q' & n' & t' & i_3 & i_4 \end{array} \right)_\kappa (T) = i^{q-q'+l-l'} \\ & \times \int \exp[-\gamma^2 - \varepsilon_a - \varepsilon_b] \gamma^2 (\varepsilon_a \varepsilon_b)^{1/2} \\ & \times 2\pi \int_0^\infty b db d(\gamma^2) d\varepsilon_a d\varepsilon_b \\ & \times \varepsilon^{i_1+i_2+i_3+i_4+(l+l'+q+q')/2} (-1)^{i_1+i_2+i_3+i_4} \\ & \times L(n, l, i_1) L(t, q, i_2) L(n', l', i_3) L(t', q', i_4) \\ & \times \left\langle x^{i_1+i_3+(l+l')/2} [y(1-x)]^{i_2+i_4+(q+q')/2} \right. \\ & \times \left. \left\{ X'(lq|l'q')_\kappa^{(0)} - \left( \frac{x'}{x} \right)^{i_1+l/2} \left[ \frac{y'(1-x')}{y(1-x)} \right]^{i_2} X'(lq|l'q')_\kappa \right\} \right\rangle \\ & \equiv \int_0^\infty \mathcal{E}^{4+i_1+i_2+i_3+i_4+(l+l'+q+q')/2} \exp(-\mathcal{E}) d\mathcal{E} \\ & \times \bar{Q}' \left( \begin{array}{cccccc} l & q & n & t & i_1 & i_2 \\ l' & q' & n' & t' & i_3 & i_4 \end{array} \right)_\kappa (E). \end{aligned} \quad (3.40)$$

Here

$$\langle \mathcal{G} \rangle = \int \mathcal{G} h(q_{K_a}; I_1^a, I_2^a) h(q_{K_b}; I_1^b, I_2^b) dR_a^{(0)} dR_b^{(0)} d\hat{r}_{K_a} d\hat{r}_{K_b}, \quad (3.41)$$

denotes the orientation average,  $x'$  and  $y'$  are the final values of  $x$  and  $y$ , respectively, and

$$\begin{aligned} \bar{Q}' & \left( \begin{array}{cccccc} l & q & n & t & i_1 & i_2 \\ l' & q' & n' & t' & i_3 & i_4 \end{array} \right)_\kappa (E) \\ & = \frac{\pi}{96} i^{l-l'+q-q'} \int_0^1 du \int_0^1 dv 2\pi \int_0^\infty b db (-1)^{i_1+i_2+i_3+i_4} \\ & \times L(n, l, i_1) L(t, q, i_2) L(n', l', i_3) L(t', q', i_4) \\ & \times \left\langle x^{i_1+i_3+(l+l')/2} [y(1-x)]^{i_2+i_4+(q+q')/2} \right. \\ & \times \left. \left\{ X'(lq|l'q')_\kappa^{(0)} - \left( \frac{x'}{x} \right)^{i_1+l/2} \left[ \frac{y'(1-x')}{y(1-x)} \right]^{i_2} X'(lq|l'q')_\kappa \right\} \right\rangle. \end{aligned} \quad (3.42)$$

The slight asymmetry in the coefficient of  $X'(lq|l'q')_\kappa$  in this equation arises because  $X'$  depends on  $(\varepsilon'_a/\varepsilon_a)^{q/2}$ , as well as on orientations. This orientation average, eqn (3.41), involves integrands of the form

$$\mathcal{I} = \int_0^{2\pi} h(q; I_x, I_y) g(q) dq, \quad (3.43)$$

where  $g(q)$  is an arbitrary function. This can be rewritten in a form more suited to Monte Carlo integration:

$$\mathcal{I} = \int_0^{2\pi} g[\bar{q}(\bar{q})] d\bar{q}, \quad (3.44)$$

where  $\tan \bar{q} = \lambda \tan q$ ,  $\lambda = \sqrt{I_x/I_y}$ ,  $0 \leq \bar{q} \leq \pi/2$ ,

and similar transformations for the rest of the  $\bar{q}$  range.

The cross section  $\bar{Q}'$  is evaluated using Monte Carlo integration in thirteen dimensions at a suitably chosen range of

total energy values, appropriate to the temperature range of interest. As in the linear-molecule code,<sup>24</sup> when evaluating this cross section each trajectory is combined with its time-reversed form. For some diagonal cross sections ( $lqnt = l'q'n't'$ ) this ensures that the integrand is positive definite. Each cross section,  $\bar{Q}'(E)$ , is then fitted to a form involving Chebyshev polynomials in  $\ln(E)$ , which allows for inexpensive evaluation of the final thermal average in eqn (3.40) at arbitrary temperatures. Finally, the lab cross section can be determined using eqn (2.27).

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