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► **To cite this version:**

Jean-Michel Launay. Molecular collision processes. I. Body-fixed theory of collisions between two systems with arbitrary angular momenta. *Journal of Physics B: Atomic and Molecular Physics*, 1977, 10 (18), pp.3665 - 3672. 10.1088/0022-3700/10/18/023 . hal-01700188

**HAL Id: hal-01700188**

**<https://hal.science/hal-01700188>**

Submitted on 28 Sep 2022

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# Molecular collision processes I. Body-fixed theory of collisions between two systems with arbitrary angular momenta

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Received 10 May 1977, in final form 13 July 1977

**Abstract.** We present a body-fixed formulation of the collision between two particles of arbitrary angular momenta. Expressions for the potential matrix elements are derived in the case where the particles are either linear molecules in  $\Sigma$  states or atoms with an active outer electron.

## 1. Introduction

In this paper we present a general formalism of the collision between two particles with arbitrary angular momenta. This is based on the body-fixed formalism for rotational excitation (Curtiss and Adler 1952, Pack 1974, Launay 1976, Rabitz 1976) and closely related to the helicity formalism (Jacob and Wick 1959, Klar 1971).

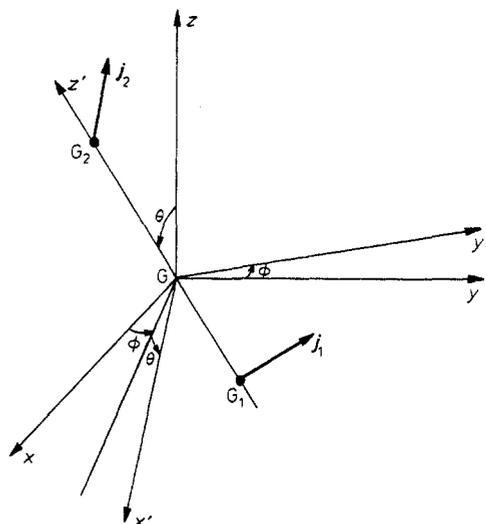
Explicit expressions are derived for the potential matrix elements in the case where the particles are either linear molecules in  $\Sigma$  states or atoms with an active outer electron (such as an excited alkali atom). We use the body-fixed expansion of the potential surfaces in terms of spherical harmonics introduced by Gioumousis and Curtiss (1961) in the case of rotational transitions in collisions between two molecules, which, as pointed out by Alexander and De Pristo (1976), is more tractable than the expansion in Legendre polynomials introduced by Davison (1962).

Limiting cases such as the rotational excitation of diatomic molecules by rare gases (Arthurs and Dalgarno 1960) or the excitation of fine-structure transitions by rare gases (Reid 1973, Mies 1973) are readily obtained.

This formalism is used in the following paper (Flower and Launay 1977b) to study the excitation of the fine-structure transition  $2p^2P_{1/2 \rightarrow 3/2}^o$  of  $C^+$  by para- and ortho- $H_2$  molecules and will subsequently be applied to calculations of rotational transitions in thermal-energy collisions between CO and  $H_2$ .

## 2. Formulation of the collision problem

We consider (figure 1) the collision between two particles 1 and 2. We denote by  $G_1$ ,  $G_2$  their respective centres of mass, and by  $G$  the centre of mass of the ensemble; the relative motion vector  $\overrightarrow{G_1G_2}$  is denoted by  $\rho$ ; the momentum and angular



**Figure 1.** The collision system. The centres of mass of the collision partners are located at  $G_1, G_2$ .  $G$  is the centre of mass of the ensemble.  $(Gxyz)$  is the space-fixed reference frame;  $(Gx'y'z')$  is the body-fixed reference frame.

momentum operators for the relative motion are  $p$  and  $l$ . In all that follows we adopt the convention of Rose (1957) for the Euler angles and rotation matrices and employ atomic units.

$(Gxyz)$  is the laboratory space-fixed (SF) frame and  $(Gx'y'z')$  is a rotating body-fixed (BF) frame.  $Gz'$  points in the direction of  $\rho$  and  $Gy'$  is chosen to lie in the  $yGz$  plane. Denoting by  $(\rho, \theta, \phi)$  the polar coordinates of  $\rho$  in the  $(Gxyz)$  frame, a rotation of Euler angles  $(\phi, \theta, 0)$  brings the  $(Gxyz)$  frame into the  $(Gx'y'z')$  frame.

The Schrödinger equation of the total system after the centre-of-mass separation can be written as

$$(\mathbf{p}^2/2\mu + H_1 + H_2 + V)|\psi\rangle = E|\psi\rangle \quad (1)$$

where  $E$  is the total energy of the system,  $\mu$  is the reduced mass of the colliding system and  $H_1, H_2$  are the Hamiltonians of the free particles.

### 2.1. Basis sets

Denoting by  $j_i$  ( $i = 1, 2$ ) the total angular momentum operators of each particle, eigenvectors for the free Hamiltonian of each particle are  $|\alpha_i j_i m_i\rangle$  and the corresponding eigenvalues are  $E_{\alpha_i j_i}$ :

$$H_i |\alpha_i j_i m_i\rangle = E_{\alpha_i j_i} |\alpha_i j_i m_i\rangle. \quad (2)$$

We then couple  $j_1$  and  $j_2$  to yield  $j_{12}$  and thus define vectors

$$|\alpha_1 j_1 \alpha_2 j_2 j_{12} m_j\rangle \equiv |\gamma j_{12} m_j\rangle$$

of energy  $E_{\alpha_1 j_1} + E_{\alpha_2 j_2}$  and where, for brevity of notation, we have put  $\gamma \equiv \alpha_1 j_1 \alpha_2 j_2$ .

Owing to the invariance of the interaction potential  $V$  under rotations of the total system and under inversions in the origin, it is convenient to write the vector solutions of (1) as a sum of different components of definite total angular momentum

$J = j_{12} + l$  and definite total parity  $\epsilon$  ( $\epsilon$  denotes the eigenvalues of  $\Pi$ , the inversion operator in the origin G). More precisely,  $J^2$ ,  $J_z$  and  $\Pi$  commute with the total Hamiltonian  $H$  and so  $J, M, \epsilon$  are conserved during the collision. Thus

$$|\psi\rangle = \sum_{JM\epsilon} |\psi^{JM\epsilon}\rangle \langle \psi^{JM\epsilon} | \psi \rangle. \quad (3)$$

The coefficients of the expansion are such that  $|\psi\rangle$  satisfies plane-wave boundary conditions, in a manner analogous to Arthurs and Dalgarno (1960). Then the  $|\psi^{JM\epsilon}\rangle$  can be expanded over a complete set of eigenvectors of  $j_{12}^2, l^2, J^2, J_z, \Pi$  formed by the usual coupling formula of angular momenta:

$$|\gamma j_{12} l JM \epsilon\rangle = \sum_{m_j m_l} |\gamma j_{12} m_j\rangle Y_{lm_l}(\theta, \phi) \langle j_{12} l m_j m_l | JM \rangle \quad (4)$$

where  $\langle ab\alpha\beta | c\gamma\rangle$  denotes a Clebsch–Gordan coefficient. The parity is  $\epsilon_{x_1 j_1} \epsilon_{x_2 j_2} (-1)^l$  where  $\epsilon_{x_i j_i}$  are the individual parities of  $|\alpha_i j_i m_i\rangle$ . The corresponding expansion may be written as

$$|\psi^{JM\epsilon}\rangle = \sum_{\gamma j_{12} l} |\gamma j_{12} l JM \epsilon\rangle \frac{1}{\rho} G_{\gamma j_{12} l}^J(\rho) \quad (5)$$

where the sum is restricted to  $\gamma, j_{12}, l$  values such that  $\epsilon = \epsilon_{x_1 j_1} \epsilon_{x_2 j_2} (-1)^l$ .

Another possibility is to expand  $|\psi^{JM\epsilon}\rangle$  over a complete set of eigenvectors of  $j_{12}^2, |j_{12z}'|, J^2, J_z, \Pi$ . We thus follow the approach of Curtiss and Adler (1952), Mies (1973), Pack (1974) and Launay (1976).

We first consider eigenfunctions of  $j_{12}^2, j_{12z}', J^2, J_z$ :

$$|\gamma j_{12} \Omega JM\rangle = |\gamma j_{12} \Omega\rangle N_{M\Omega}^J(\theta, \phi) \quad (6)$$

where

$$N_{M\Omega}^J(\theta, \phi) = [(2J + 1)/4\pi]^{1/2} D_{M\Omega}^{J*}(\phi, \theta, 0)$$

are normalised symmetric-top wavefunctions and  $D$  is a rotation matrix (Rose 1957).

Eigenvectors of definite parity  $\epsilon$  are obtained from a linear combination of the  $+\Omega$  and  $-\Omega$  components. Denoting  $\bar{\Omega} = |\Omega|$ , we get (see appendix 1)

$$|\gamma j_{12} \bar{\Omega} JM \epsilon\rangle = (|\gamma j_{12} \bar{\Omega} JM\rangle + \epsilon p |\gamma j_{12} - \bar{\Omega} JM\rangle) [2^{1/2} (1 + \epsilon p \delta_{\bar{\Omega} 0})^{1/2}]^{-1} \quad (7)$$

where

$$p = \epsilon_{x_1 j_1} \epsilon_{x_2 j_2} (-1)^{J - j_{12}}.$$

The relation between the two sets of eigenvectors (4) and (7) is a unitary transformation  $P^{J\epsilon}$  (see appendix 1):

$$|\gamma j_{12} l JM \epsilon\rangle = \sum_{\bar{\Omega}} P_{l\bar{\Omega}}^{\gamma j_{12}; J\epsilon} |\gamma j_{12} \bar{\Omega} JM \epsilon\rangle \quad (8)$$

where

$$P_{l\bar{\Omega}}^{\gamma j_{12}; J\epsilon} = \left( \frac{2(2l + 1)}{(1 + \epsilon p \delta_{\bar{\Omega} 0})(2J + 1)} \right)^{1/2} \langle j_{12} l \bar{\Omega} 0 | J \bar{\Omega} \rangle. \quad (9)$$

### 3. Scattering equations

We expand  $|\psi^{JM\epsilon}\rangle$  in the set of eigenvectors (7):

$$|\psi^{JM\epsilon}\rangle = \sum_{\gamma j_{12}\bar{\Omega}} |\gamma j_{12}\bar{\Omega} JM\epsilon\rangle \frac{1}{\rho} G_{\gamma j_{12}\bar{\Omega}}^{J\epsilon}(\rho) \quad (10)$$

and use

$$p^2 = -\frac{1}{\rho} \frac{\partial^2}{\partial \rho^2} \rho + l^2/\rho^2.$$

We thus get a set of coupled second-order differential equations:

$$\frac{d^2}{d\rho^2} G_{\gamma j_{12}\bar{\Omega}}^{J\epsilon}(\rho) + \sum_{\gamma' j'_{12}\bar{\Omega}'} W_{\gamma j_{12}\bar{\Omega}; \gamma' j'_{12}\bar{\Omega}'}^{J\epsilon}(\rho) G_{\gamma' j'_{12}\bar{\Omega}'}^{J\epsilon}(\rho) = 0 \quad (11)$$

where

$$W_{\gamma j_{12}\bar{\Omega}; \gamma' j'_{12}\bar{\Omega}'}^{J\epsilon}(\rho) = \delta_{\gamma\gamma'} \delta_{j_{12}j'_{12}} \delta_{\bar{\Omega}\bar{\Omega}'} k_\gamma^2 - \frac{1}{\rho^2} \langle \gamma j_{12}\bar{\Omega} JM\epsilon | l^2 | \gamma' j'_{12}\bar{\Omega}' JM\epsilon \rangle - 2\mu \langle \gamma j_{12}\bar{\Omega} JM\epsilon | V | \gamma' j'_{12}\bar{\Omega}' JM\epsilon \rangle. \quad (12)$$

In (12),  $k_\gamma$  is the wavenumber defined by  $k_\gamma^2 = 2\mu(E - E_{x_1j_1} - E_{x_2j_2})$ ;  $l^2$  is diagonal in the  $\gamma j_{12}$  indices; formulae for the matrix elements are given in appendix 2.

The interaction potential  $V$  is diagonal in the  $\bar{\Omega}$  index due to its invariance under rotations about  $\rho$ . A general formula, valid when the particles are either linear  $\Sigma$  molecules or atoms with an active outer electron is given in appendix 3. Then the interaction potential between the two particles may be written as

$$V(\hat{R}_1, \hat{R}_2, \rho) = \sum_{q_1 q_2 \mu} v_{q_1 q_2 \mu}(\rho) Y_{q_1 q_2 \mu}(\hat{R}_1, \hat{R}_2) \quad (13)$$

where  $\hat{R}_1, \hat{R}_2$  are the body-fixed angular coordinates of the electron or of the molecule and

$$Y_{q_1 q_2 \mu}(\hat{R}_1, \hat{R}_2) = 4\pi [Y_{q_1 \mu}(\hat{R}_1) Y_{q_2 - \mu}(\hat{R}_2) + Y_{q_1 - \mu}(\hat{R}_1) Y_{q_2 \mu}(\hat{R}_2)] [2(1 + \delta_{\mu 0})]^{-1/2} \quad (14)$$

( $0 \leq \mu \leq \min(q_1, q_2)$ ) are a set of real operators invariant under rotations about the  $\rho$  axis and under reflections through a plane containing  $\rho$ . They obey the following normalisation properties:

$$\int Y_{q_1 q_2 \mu}(\hat{R}_1, \hat{R}_2) Y_{q_1 q_2 \mu'}(\hat{R}_1, \hat{R}_2) d\hat{R}_1 d\hat{R}_2 = 16\pi^2 \delta_{q_1 q_1'} \delta_{q_2 q_2'} \delta_{\mu \mu'}. \quad (15)$$

If particle 2 is spherically symmetric, we have  $q_2 = \mu = 0$  and we obtain  $Y_{q_1 0 0}(\hat{R}_1, \hat{R}_2) = (2q_1 + 1)^{1/2} P_{q_1}(\cos \theta_1)$  where  $\cos \theta_1 = \hat{R}_1 \cdot \hat{\rho}$ .

We thus have the usual expansion over Legendre polynomials which was used by Arthurs and Dalgarno (1960) for rotational excitation and by Reid (1973) for fine-structure transitions. A potential of the form (13) has been derived by Flower and Launay (1977a) for the interaction of  $C^+(2p^2P^o)$  with  $H_2$  from available potential energy surfaces (Liskow *et al* 1974).

Matrix elements may then be written as

$$\langle \gamma j_{12}\bar{\Omega} JM\epsilon | V | \gamma' j'_{12}\bar{\Omega}' JM\epsilon \rangle = \sum_{q_1 q_2 \mu} v_{q_1 q_2 \mu}(\rho) c_{\gamma j_{12}\bar{\Omega}; \gamma' j'_{12}\bar{\Omega}'}^{q_1 q_2 \mu}. \quad (16)$$

where

$$c_{\gamma j_{12} \bar{\Omega}; \gamma' j'_{12} \bar{\Omega}'}^{q_1 q_2 \mu} = \langle \gamma j_{12} \bar{\Omega} J M \epsilon | Y_{q_1 q_2 \mu} | \gamma' j'_{12} \bar{\Omega}' J M \epsilon \rangle$$

is an algebraic coefficient which is independent of the quantum numbers  $J, M, \epsilon$ . The explicit form, when each particle obeys an  $LS$ -coupling scheme, is given in appendix 3.

### 3.1. Numerical procedure

A large number of elements of the  $W^{J\epsilon}(\rho)$  matrix are zero. Full account is taken of this fact to reduce the computational time in the De Vogelaere (1955) algorithm (Launay 1976). This proves to be very effective when we deal with large ( $\geq 10$ ) numbers of equations.

### 3.2. Boundary conditions

The  $N$  scattering equations (11) are solved for a square  $N \times N$  matrix  $G_{\text{BF}}^{J\epsilon}(\rho)$  of linearly independent solutions satisfying the usual boundary condition at the origin  $G_{\text{BF}}^{J\epsilon}(0) = 0$ . This matrix is then converted to the SF representation at a distance which is sufficiently far in the asymptotic region by means of the relation:

$$G_{\text{SF}}^{J\epsilon}(\rho) = P^{J\epsilon} G_{\text{BF}}^{J\epsilon}(\rho) P^{J\epsilon\dagger}$$

$P^{J\epsilon}$  being the matrix of the unitary transformation (9). This matrix is then matched to diagonal matrices of spherical Bessel functions of the first and second kinds  $j_l$  and  $n_l$  (Abramowitz and Stegun 1965):

$$G_{\text{SF}}^{J\epsilon}(\rho) \sim J^{J\epsilon}(\rho) A^{J\epsilon} - N^{J\epsilon}(\rho) B^{J\epsilon}$$

where

$$J_{\gamma j_{12}; \gamma' j'_{12}}^{J\epsilon}(\rho) = \delta_{\gamma\gamma'} \delta_{j_{12} j'_{12}} \delta_{ll'} k_{\gamma}^{1/2} \rho j_l(k_{\gamma} \rho)$$

$$N_{\gamma j_{12}; \gamma' j'_{12}}^{J\epsilon}(\rho) = \delta_{\gamma\gamma'} \delta_{j_{12} j'_{12}} \delta_{ll'} k_{\gamma}^{1/2} \rho n_l(k_{\gamma} \rho).$$

The  $K^{J\epsilon}$  and  $T^{J\epsilon}$  matrices are then obtained using

$$K^{J\epsilon} = B^{J\epsilon} (A^{J\epsilon})^{-1}$$

$$T^{J\epsilon} = -2iK^{J\epsilon} (1 - iK^{J\epsilon})^{-1}.$$

Partial cross sections averaged over initial states and summed over final states for transitions from  $\gamma'$  to  $\gamma$  are given by

$$\sigma_{\gamma' \rightarrow \gamma}^J = \frac{\pi(2J+1)}{k_{\gamma'}^2 \omega(\gamma')} \sum_{j_{12} j'_{12} l \epsilon} |T_{\gamma j_{12}; \gamma' j'_{12}}^{J\epsilon}|^2$$

where  $\omega(\gamma') = (2j'_1 + 1)(2j'_2 + 1)$  is the degeneracy of the initial state  $\gamma'$ .

Total cross sections are given by

$$\sigma_{\gamma' \rightarrow \gamma} = \sum_{J=0}^{\infty} \sigma_{\gamma' \rightarrow \gamma}^J.$$

### Acknowledgments

I would like to thank D Flower for his continuing interest in this work.

### Appendix 1. Unitary transformation

We shall consider the space-fixed wavefunctions  $|\gamma j_{12} l J M \epsilon\rangle$  as being constructed from the spherical harmonics  $Y_{lm_l}(\theta, \phi)$  describing the relative movement of the particles and from the molecular wavefunctions  $|\gamma j_{12} \Omega\rangle_{\text{BF}}$  describing the internal motions.

We have

$$|\gamma j_{12} l J M \epsilon\rangle = \sum_{m_j, m_l, \Omega} D_{m_j \Omega}^{j_{12} l*}(\phi, \theta, 0) |\gamma j_{12} \Omega\rangle_{\text{BF}} Y_{lm_l}(\theta, \phi) \langle j_{12} l m_j m_l | J M \rangle \quad (\text{A.1})$$

which gives, when using the relation between spherical harmonics and rotation matrices:

$$Y_{lm_l}(\theta, \phi) = \left( \frac{2l+1}{4\pi} \right)^{1/2} D_{m_l 0}^l(\phi, \theta, 0)$$

and the composition theorem of rotation matrices:

$$\begin{aligned} \sum_{m_j, m_l} \langle j_{12} l m_j m_l | J M \rangle D_{m_j 0}^{j_{12} l*} D_{m_l \Omega}^{j_{12} l*} &= \langle j_{12} l \Omega 0 | J \Omega \rangle D_{M \Omega}^{J*} \\ |\gamma j_{12} l J M \epsilon\rangle &= \sum_{\Omega} \left( \frac{2l+1}{2J+1} \right)^{1/2} \langle j_{12} l \Omega 0 | J \Omega \rangle |\gamma j_{12} \Omega J M \rangle. \end{aligned} \quad (\text{A.2})$$

Using the unitarity property of this transformation, we can write:

$$|\gamma j_{12} \Omega J M \rangle = \sum_{\Gamma} \left( \frac{2l+1}{2J+1} \right)^{1/2} \langle j_{12} l \Omega 0 | J \Omega \rangle |\gamma j_{12} l J M \epsilon \rangle. \quad (\text{A.3})$$

We consider now the effect of  $\Pi$ , the inversion operator, on both sides of (A.3). We have easily:

$$\Pi |\gamma j_{12} l J M \epsilon \rangle = \epsilon_{\alpha_1 j_1} \epsilon_{\alpha_2 j_2} (-1)^l |\gamma j_{12} l J M \epsilon \rangle \quad (\text{A.4})$$

and using

$$\langle j_{12} l \Omega 0 | J \Omega \rangle = (-1)^{J-j_{12}+l} \langle j_{12} l - \Omega 0 | J - \Omega \rangle$$

we get:

$$\Pi |\gamma j_{12} \Omega J M \rangle = \epsilon_{\alpha_1 j_1} \epsilon_{\alpha_2 j_2} (-1)^{J-j_{12}} |\gamma j_{12} - \Omega J M \rangle. \quad (\text{A.5})$$

The functions  $|\gamma j_{12} \Omega J M \rangle + \epsilon \Pi |\gamma j_{12} \Omega J M \rangle$  have parity  $\epsilon$  and norm  $[2(1 + \epsilon p \delta_{\bar{\Omega} 0})]^{1/2}$  with  $p = \epsilon_{\alpha_1 j_1} \epsilon_{\alpha_2 j_2} (-1)^{J-j_{12}}$  and thus we have:

$$|\gamma j_{12} \bar{\Omega} J M \epsilon \rangle = (|\gamma j_{12} \bar{\Omega} J M \rangle + \epsilon p |\gamma j_{12} - \bar{\Omega} J M \rangle) [2^{1/2}(1 + \epsilon p \delta_{\bar{\Omega} 0})^{1/2}]^{-1}. \quad (\text{A.6})$$

Using (A.2) and (A.6), we easily get the unitary transformation given by (8) and (9).

## Appendix 2. $I^2$ matrix elements

We first evaluate  $I^2$  matrix elements in the  $|\gamma j_{12} \Omega JM\rangle$  basis. The derivation is the same as in Launay (1976). Non-zero matrix elements are given by

$$\begin{aligned} \langle \gamma j_{12} \Omega JM | I^2 | \gamma j_{12} \Omega \pm 1 JM \rangle &= -\alpha_{\pm}(j_{12}, \Omega) \alpha_{\pm}(J, \Omega) \\ \langle \gamma j_{12} \Omega JM | I^2 | \gamma j_{12} \Omega JM \rangle &= \beta(j_{12}, J, \Omega) \end{aligned} \quad (\text{A.7})$$

where

$$\begin{aligned} \alpha_{\pm}(a, b) &= [a(a+1) - b(b \pm 1)]^{1/2} \\ \beta(a, b, c) &= a(a+1) + b(b+1) - 2c^2. \end{aligned}$$

$I^2$  matrix elements in the  $|\gamma j_{12} \bar{\Omega} JM \epsilon\rangle$  basis are obtained using formula (A.6). Explicit expressions (valid whether  $j_{12}$  is integer or half-integer) are:

$$\begin{aligned} \langle \gamma j_{12} \bar{\Omega} JM \epsilon | I^2 | \gamma j_{12} \bar{\Omega} \pm 1 JM \epsilon \rangle &= -(1 + \epsilon p \delta_{\bar{\Omega} 0})^{1/2} \alpha_{\pm}(j_{12}, \bar{\Omega}) \alpha_{\pm}(J, \bar{\Omega}) \\ \langle \gamma j_{12} \bar{\Omega} JM \epsilon | I^2 | \gamma j_{12} \bar{\Omega} JM \epsilon \rangle &= \beta(j_{12}, J, \bar{\Omega}) - \epsilon p \delta_{\bar{\Omega} \frac{1}{2}} \alpha_{-}(j_{12}, \bar{\Omega}) \alpha_{-}(J, \bar{\Omega}). \end{aligned} \quad (\text{A.8})$$

## Appendix 3. $V$ -matrix elements

We shall assume that each particle has an orbital angular momentum  $L_i$  and a spin angular momentum  $S_i$  which couple to give  $j_i = L_i + S_i$ . We assume that we have pure  $LS$  coupling so that the vectors  $|\alpha_i j_i m_i\rangle$  may be labelled as  $|(L_i S_i) j_i m_i\rangle$  and thus  $\gamma \equiv L_1 S_1 L_2 S_2$ .

The algebraic coefficients in equation (16) are given by:

$$c_{\gamma j_{12} \bar{\Omega}; \gamma' j_{12} \bar{\Omega}'}^{q_1 q_2 \mu} = \langle \gamma j_{12} \bar{\Omega} JM \epsilon | Y_{q_1 q_2 \mu}(\hat{R}_1, \hat{R}_2) | \gamma' j_{12} \bar{\Omega}' JM \epsilon \rangle_{\hat{R}_1, \hat{R}_2, \hat{\rho}} \quad (\text{A.9})$$

where the index in the scalar product denotes the integration over  $\hat{R}_1, \hat{R}_2, \hat{\rho}$ . Using equations (6), (7) and the normalisation properties of the symmetric-top wavefunction, we obtain

$$c_{\gamma j_{12} \bar{\Omega}; \gamma' j_{12} \bar{\Omega}'}^{q_1 q_2 \mu} = \langle \gamma j_{12} \bar{\Omega} | Y_{q_1 q_2 \mu}(\hat{R}_1, \hat{R}_2) | \gamma' j_{12} \bar{\Omega}' \rangle_{\hat{R}_1, \hat{R}_2}. \quad (\text{A.10})$$

The functions  $Y_{q_1 q_2 \mu}(\hat{R}_1, \hat{R}_2)$  are expanded over a basis of irreducible tensorial operators:

$$\begin{aligned} Y_{q_1 q_2 \mu}(\hat{R}_1, \hat{R}_2) &= \sum_{q_{12}} (-1)^{q_1 + q_2} \left( \frac{2(2q_{12} + 1)}{1 + \delta_{\mu 0}} \right)^{1/2} \begin{pmatrix} q_1 & q_2 & q_{12} \\ -\mu & \mu & 0 \end{pmatrix} \\ &\times 4\pi \{ Y_{q_1}(\hat{R}_1) \times Y_{q_2}(\hat{R}_2) \}_{q_{12} 0} \end{aligned} \quad (\text{A.11})$$

where  $\begin{pmatrix} abc \\ x\beta\gamma \end{pmatrix}$  are  $3j$  coefficients, and where the sum is over  $q_{12}$  values of the same parity as  $q_1 + q_2$ .

By application of the Wigner–Eckart theorem and of Racah algebraic techniques (Messiah 1964), we get straightforwardly

$$\begin{aligned}
 c_{j_1 j_2 \Omega; j'_1 j'_2 \Omega'}^{q_1 q_2 \mu} &= \delta_{\Omega \Omega'} \delta_{S_1 S_1'} \delta_{S_2 S_2'} (-1)^{S_1 + j_1 + S_2 + j_2 + j_{12} - \Omega} \left( \frac{2}{1 + \delta_{\mu 0}} \right)^{1/2} \\
 &\times \{j_1, j_2, j_{12}, j'_1, j'_2, j'_{12}, L_1, q_1, L'_1, L_2, q_2, L'_2\}^{1/2} \\
 &\times \begin{pmatrix} L_1 & q_1 & L'_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_2 & q_2 & L'_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L_1 & j_1 & S_1 \\ j'_1 & L_1 & q_1 \end{Bmatrix} \\
 &\times \begin{Bmatrix} L_2 & j_2 & S_2 \\ j'_2 & L'_2 & q_2 \end{Bmatrix} \sum_{q_{12}} (2q_{12} + 1) \begin{pmatrix} q_1 & q_2 & q_{12} \\ -\mu & \mu & 0 \end{pmatrix} \begin{pmatrix} j_{12} & q_{12} & j'_{12} \\ -\Omega & 0 & \Omega \end{pmatrix} \\
 &\times \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j'_1 & j'_2 & j'_{12} \\ q_1 & q_2 & q_{12} \end{Bmatrix} \tag{A.12}
 \end{aligned}$$

where  $\{a, b, c, \dots\} = (2a + 1)(2b + 1)(2c + 1) \dots$ , and  $\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix}$

are  $6j$  and  $9j$  coefficients.

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