Quantum theory of angular momentum coupling in reactive collisions*

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Quantum scattering theories of chemical reaction usually require, at some stage, a transformation from the quantum states of reactants to those of the products. We show that it is useful to separate this transformation into angular momentum coefficients and translational–vibrational integrals. The angular momentum coefficients thus defined are general kinematic factors, depending only on the masses of the atoms and the product vibrational and translational distances, but not on the particular potential surface. Analytic formulas are derived for these angular momentum coefficients, both for reactions confined to a plane and for three-dimensional motion. Various selection rules, symmetry properties, orthogonality conditions, normalization rules, and recursion relations are derived from these formulas. An efficient and numerically stable method is derived for numerical evaluation of the angular momentum coefficients. Examples are given for several specific reactions and the trends with varying mass combinations are rationalized in terms of limiting cases. These results display the kinematic aspects of angular momentum transfer in chemical reactions. Comparison with classical trajectories, which include both dynamic and kinematic effects, shows the extent to which dynamic effects alter the distributions of rotational and orbital angular momenta from those given by the kinematic effects alone. Finally, the integral for the transformation of the vibrational and radial dependence of the scattering wavefunction is discussed qualitatively.

I. INTRODUCTION

Molecular beam measurements of total reaction cross sections and of product angular distributions have provided a great deal of information about elementary chemical reactions of the type $A + BC \rightarrow AB + C$. Recent developments of molecular beam techniques allow one to measure the orientational distribution of the product rotational states. Spectroscopic techniques now can determine the distribution of product rotational and vibrational energies. These measurements call for new, more detailed theoretical studies of molecular reactions.

Classical and semiclassical calculations have been most successful in describing reactive molecular scattering. In this paper, we will be concerned with developing further the quantum mechanical theory of reactive collisions. Quantum mechanical calculations have been carried out mainly on collinear reactions, but no general method exists so far to deal with reactions not restricted to a collinear configuration of the nuclei involved. Because of the long range character of molecular interactions, chemical reactions often involve large angular momentum values. Therefore, as well as in the light of the recent molecular beam measurements, it is necessary to extend the calculations to include the rotational degrees of freedom,[1] and the orbital angular momentum.

In reactive collisions with sticky collision complexes, all degrees of freedom are sufficiently coupled to populate all open product channel states significantly. Statistical models therefore are reasonable in describing the outcome of these collisions.[2a] If reactions, however, proceed via a loose, very short-lived transition complex, the population of product channel states deviates from a statistical distribution. In such cases the rotational degrees of freedom will often be only weakly coupled to the translational and vibrational degrees of freedom; hence, the population of product rotational states will reflect to an important degree the reactant rotational states altered by the redistribution of masses in the reactive event.[2b,3]

In these "direct" reactions, the transformation that connects reactant and product rotational states strongly influences the product angular momentum distributions. The matrix elements of the transformation that couples reactant and product angular momentum states depend both on the shape of the reaction complex and on the masses of the colliding particles. In this paper we derive analytical expressions for these reactant–product angular momentum coupling coefficients. Since the transformation considered is independent of the actual dynamics of the reactive system, the coupling coefficients derived are applicable for all reactive scattering calculations.

In Sec. II we introduce the connection of the reactant–product transformation of angular momentum states with several formal approaches for three particle reactive scattering. In Sec. III the angular momentum rearrangement transformation for reactions restricted to a plane is derived, and the derivation is extended in Sec. IV to three-dimensional reactions. In Sec. V some numerical examples of reactant–product angular momentum coupling coefficients are presented for some sample reactions and quasiselection rules for product rotational states which follow from our coupling scheme are compared with the results of classical trajectory calculations. In Sec. VI we discuss the reactant–product integral transformations for the translational–vibrational wavefunctions which necessarily accompany the transformations of the angular momentum wavefunctions in any detailed calculations.

We have also developed a suitable algorithm for the numerical evaluation of the reactant–product coupling matrix elements. It produces accurate results effi-
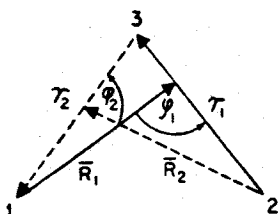
FIG. 1. Definition of coordinates for the arrangements 1 + (2, 3) and 2 + (1, 3).

ciently, even for very large angular momentum quantum numbers (> 100), which are present in many reactions. In Appendix A we describe this algorithm for the new class of coupling coefficients that are derived in this paper, and in Appendix C we present an algorithm for the evaluation of $9j$ coefficients for large angular momenta, which are needed in the course of our calculations.

II. SOLUTIONS OF NONREACTIVE AND REACTIVE SCATTERING

In the following we will consider three colliding particles in their center-of-mass (c. m.) system. To describe a collision of particle 1 with the bound pair of particles (2, 3), one can choose coordinates R_1 and r_1 defined in Fig. 1. R_1 goes from particle 1 to the center of mass of the (2, 3) subsystem; r_1 connects particle 2 with particle 3. It will be more convenient to use rescaled coordinates,[4] N_1 and n_1, which are related to R_1 and r_1 by

$$N_1 = \alpha_1^{-1} R_1 ,$$

$$n_1 = \alpha_1 r_1 , \tag{1}$$

$$\alpha_1^2 = [m_2 m_3 (m_1 + m_2 + m_3)/m_1 (m_2 + m_3)^2]^{1/2} .$$

Coordinates (N_1, n_1) and (N_2, n_2) describing two different arrangements of the particles (see Fig. 1) are then connected by the simple transformation formulas

$$N_1 = \cos\beta N_2 - \sin\beta\, n_2 , \tag{2a}$$

$$n_1 = \sin\beta N_2 + \cos\beta\, n_2 , \tag{2b}$$

where $\cos\beta = -[m_1 m_2/(m_1 + m_3)(m_2 + m_3)]^{1/2}$ and $\sin\beta > 0$.

The momentum vectors $P_i = \mu \dot{N}_i$ and $p_i = \mu \dot{n}_i$ $(i = 1, 2)$ with $\mu = [m_1 m_2 m_3/(m_1 + m_2 + m_3)]^{1/2}$ transform like the position vectors.

A wavefunction ψ which describes the inelastic but nonreactive collisions $1 + (2, 3) \rightarrow 1 + (2, 3)^*$ is a regular eigenfunction of the three-particle Hamiltonian H. As atom 1 separates from molecule (2, 3), ψ must go asymptotically $(N_1 \rightarrow \infty)$ to

$$\psi_1 = \sum_{L, l, n} f^{(1)}_{Lln}(N_1) v^{(1)}_{nl}(n_1) \mathcal{Y}_{JM}(L, l; \hat{N}_1, \hat{n}_1) . \tag{3}$$

In this expansion, $f^{(1)}_{Lln}(N_1)$ describes a free translation between atom 1 and molecule (2, 3),

$$f^{(1)}_{Lln}(N_1) = \frac{1}{\sqrt{k_{ln}}} (j_L(k_{ln} N_1) - n_L(k_{ln} N_1) R_{Lln}) . \tag{4}$$

$v^{(1)}_{nl}(n_1)$ describes the vibration of molecule (2, 3) in its lth rotational state, and $\mathcal{Y}_{JM}(L, l; \hat{N}_1, \hat{n}_1)$, defined by

$$\mathcal{Y}_{JM}(L, l; \hat{N}_1, \hat{n}_1) = \sum_{m_L m_l} (L m_L l m_l | JM) Y_{L m_L}(\hat{N}_1) Y_{l m_l}(\hat{n}_1) \tag{5}$$

describes the total angular momentum state (J, M) of the atom–molecule system with orbital angular momentum L and molecular (rotational) angular momentum l. $\hat{N}_1$ and $\hat{n}_1$ stand for the angles that define the directions of N_1 and n_1, respectively. $(L m_L l m_l | JM)$ denotes the Clebsch–Gordan coefficient as defined in Edmonds.[5] ψ_1 is a solution of $(H_0^{(1)} - E)\psi_1 = 0$, where $H_0^{(1)} = \lim_{N_1 \to \infty} H$, and E is the total energy of the three particles in their c. m. system.

To insure the right asymptotic behavior, the inelastic scattering solution ψ is expressed in terms of the partial waves that contribute to ψ_1,

$$\psi = \sum_{L, l, n} F^{(1)}_{Lln}(N_1) v^{(1)}_{nl}(n_1) \mathcal{Y}_{JM}(L, l; \hat{N}_1, \hat{n}_1) . \tag{6}$$

The translational wavefunctions $F^{(1)}_{Lln}(N_1)$ have to be determined from the set of coupled ordinary differential equations

$$\sum_{L', l', n'} \int d\hat{N}_1 \int d n_1 v^{(1)}_{nl}(n_1) \mathcal{Y}^*_{JM}(L, l; \hat{N}_1, \hat{n}_1)(H - E)$$

$$\times v^{(1)}_{n'l'}(n_1) \mathcal{Y}_{JM}(L', l'; \hat{N}_1, \hat{n}_1) F^{(1)}_{L'l'n'}(N_1) = 0 . \tag{7}$$

Methods to solve this equation are by now well known.[6] If the angular dependence of the potential is expanded in Legendre polynomials P_s,

$$V(N_1, n_1, \phi_1) = \sum_s V_s(N_1, n_1) P_s(\cos\phi_1) , \tag{8}$$

then the matrix elements

$$\langle \mathcal{Y}_{JM}(L, l; \hat{N}_1, \hat{n}_1) | P_s(\cos\phi_1) | \mathcal{Y}_{JM}(L', l', \hat{N}_1, \hat{n}_1) \rangle \tag{9}$$

appear as factors in each term of Eq. (7). On application of the Racah algebra of angular momentum coupling, these matrix elements can be expressed in terms of vector coupling coefficients.[7] The angular momentum coupling factors (9) strongly affect the results of inelastic scattering calculations and establish selection rules for the collisional transitions.

In case of weak coupling between rotational states, the distorted wave Born approximation (DWBA) can be applied; the transition amplitudes are found in this case to be directly proportional to the corresponding angular momentum coupling coefficients (9). The transition amplitudes deviate from this behavior if the coupling between rotational states is somewhat stronger, and transitions can occur via intermediate channels. However, the angular momentum coupling coefficients still determine to first order the relative magnitude of the transition amplitudes. In case of strong coupling the transitions through intermediate channels become as important as direct transitions; then the angular momentum coupling coefficients no longer provide an estimate for the transition amplitudes. These considerations will hold equally for transitions connecting reactant and product states in case of reactive collisions, for which the angular momentum coupling coefficients are derived in this paper.

Let us now consider collisions for which reactive channels are energetically accessible in the asymptotic region so that both the inelastic processes $1 + (2, 3) \rightarrow 1 + (2, 3)^*$ and the reactive processes $1 + (2, 3) \rightarrow 2 + (1, 3)^*$

are energetically allowed. The reaction products $(1, 3)^*$ and 2 are described asymptotically by the wave-function

$$\psi_2 = \sum_{L, l, n} F^{(2)}_{L, l, n}(N_2) v^{(2)}_{nl}(n_2) y_{JM}(L, l; \hat{N}_2, \hat{n}_2) . \quad (10)$$

The functions occurring in this expansion have the same meaning as those defining ψ_1. The wavefunction ψ, in order to represent reactive collision processes $1 + (2, 3) \rightarrow 2 + (1, 3)^*$, has to be subject to *two* asymptotic boundary conditions,

$$\psi \xrightarrow[N_1 \text{ large}]{} \psi_1$$

$$\qquad\qquad\qquad\qquad (11)$$

$$\psi \xrightarrow[N_2 \text{ large}]{} \psi_2 .$$

The N_1 axis and the N_2 axis point towards different directions in the three-particle configuration space and, hence, the boundary conditions force the scattering wavefunction ψ to have nonvanishing asymptotic tails ψ_1 and ψ_2 confined along two different directions. The difficulties encountered in reactive scattering calculations stem from the difficulty of satisfying these boundary conditions. In the case that the particles are restricted to collinear reactions, the difficulties can be overcome by evaluating ψ in a configuration space transformed such that the reactant and product coordinates N_1 and N_2 and, hence, the asymptotic waves ψ_1 and ψ_2, come to run parallel in the asymptotic region.[8] Similar transformations employed for three-dimensional reactive processes which connect both asymptotic arrangements of the particles, $1 + (2, 3)$ and $2 + (1, 3)$, lead to complicated forms of the kinetic energy operator.[9a] Quantum mechanical calculations using such coordinate systems (limited, however, to reactions with nearly collinear collision complexes) have been proposed recently.[9b]

Boundary conditions (11) will automatically be satisfied if one expands

$$\psi = \sum_{L, l, n} F^{(1)}_{Lln}(N_1) v^{(1)}_{nl}(n_1) y_{JM}(L, l; \hat{N}_1, \hat{n}_1)$$

$$\quad + \sum_{L', l', n'} F^{(2)}_{L'l'n'}(N_2) v^{(2)}_{n'l'}(n_2) y_{JM}(L', l'; \hat{N}_2, \hat{n}_2) . \quad (12)$$

The unknown reactant and product translational wavefunctions $F^{(1)}_{Lln}(N_1)$ and $F^{(2)}_{L'l'n'}(N_2)$ can be found as solutions of the two-dimensional coupled integro-differential equations

$$\sum_{\beta, L', l', n'} \int d\hat{N}_\alpha \int d\hat{n}_\alpha y^*_{JM}(L, l; \hat{N}_\alpha, \hat{n}_\alpha)(H - E)$$

$$\times y_{JM}(L', l'; \hat{N}_\beta, \hat{n}_\beta) F^{(\beta)}_{L'l'n'}(N_\beta) v^{(\beta)}_{n'l'}(n_\beta) = 0 . \quad (13)$$

The terms multiplying $F^{(\alpha)}_{L'l'n'}(N_\alpha)$ $(\alpha = \beta)$ are evaluated in the same manner as the corresponding terms occurring in the inelastic scattering Eq. (7), except that the

integration in (13) is not extended over the vibrational wavefunctions $v^{(\alpha)}_{nl}(n_\alpha)$. The angular momentum coupling for these terms follows the scheme employed for inelastic collisions.

The terms acting on $F^{(\beta)}_{L'l'n'}(N_\beta)$ with $\alpha \neq \beta$ cause the coupling of reactant and product channels. The evaluation of these terms is very different from the evaluation of the terms with $\alpha = \beta$. First, the matrix elements that couple the angular parts of the wavefunctions,

$$\langle y_{JM}(L, l; \hat{N}_\alpha, \hat{n}_\alpha) | P_s(\cos\phi_2) | y_{JM}(L', l'; \hat{N}_\beta, \hat{n}_\beta) \rangle , \quad (14)$$

cannot be determined within the Racah algebra of ordinary angular momentum coupling. Second, the integration over the solid angles $\hat{N}_\alpha$ and $\hat{n}_\alpha$ extends over the unknown translational wavefunctions $F^{(\beta)}_{L'l'n'}(N_\beta)$. This gives rise to the well-known nonlocal character of the reactive scattering Schrödinger equation, when its solution is expanded in both reactant and product bases, as in Eq. (12).[1]

To evaluate formally the reactant–product coupling terms, the partial wave

$$F^{(\beta)}_{L'l'n'}(N_\beta) v^{(\beta)}_{n'l'}(n_\beta) y_{JM}(L', l'; \hat{N}_\beta, \hat{n}_\beta)$$

is transformed to the coordinates N_α and n_α. The total angular momentum state in the β arrangement is therefore recoupled and expressed in terms of total angular momentum states of the α arrangement,

$$y_{JM}(L, l; \hat{N}_\beta, \hat{n}_\beta)$$

$$= \sum_{L', l'} {}_3 C^J_{Ll; L'l'}(N_\alpha, n_\alpha) y_{JM}(L', l'; \hat{N}_\alpha, \hat{n}_\alpha) . \quad (15)$$

The functional dependence on N_α and n_α of the recoupling coefficients ${}_3 C^J_{Ll; L''l''}(N_\alpha, n_\alpha)$ takes into account the fact that the rotational modes of motion in the β arrangement contain some component of translational–vibrational motion in the α arrangements. The translational–vibrational terms in (12) describing the β arrangement in turn contain some component of *internal* angular motion in the α arrangement:

$$F^{(\beta)}_{L'l'n'}(N_\beta) v^{(\beta)}_{n'l'}(n_\beta)$$

$$= \sum_t \mathcal{F}^{(\beta)}_{L'l'n';t}(N_\alpha, n_\alpha) y_{00}(t, t; \hat{N}_\alpha, \hat{n}_\alpha) . \quad (16)$$

The analytical form of the recoupling coefficients ${}_3 C^J_{L'l'; L''l''}(N_\alpha, n_\alpha)$ will be derived in Secs. III and IV. The derivation will employ a coupling scheme for angular momentum states which is based on the theory of the representation of the Euclidean group rather than the rotation group. The evaluation of the functions $\mathcal{F}^{(\beta)}_{L'l'n';t}(N_\alpha, n_\alpha)$ will be discussed in Sec. VI.

On application of the transformations (15) and (16), the Schrödinger equation reads

$$\sum_{L', l', n'} \int d\hat{N}_\alpha \int d\hat{n}_\alpha y^*_{JM}(L, l; \hat{N}_\alpha, \hat{n}_\alpha)(H - E) y_{JM}(L', l'; \hat{N}_\alpha, \hat{n}_\alpha) F^{(\alpha)}_{L'l'n'}(N_\alpha) v^{(\alpha)}_{n'l'}(N_\alpha)$$

$$+ \sum_{\substack{L', l', n' \\ L'', l'', t}} \int d\hat{N}_\alpha \int d\hat{n}_\alpha y^*_{JM}(L, l; \hat{N}_\alpha, \hat{n}_\alpha)(H - E) y_{JM}(L'', l''; \hat{N}_\alpha, \hat{n}_\alpha) y_{00}(t, t; \hat{N}_\alpha, \hat{n}_\alpha) \mathcal{F}^{(\beta)}_{L'l'n';t}(N_\alpha, n_\alpha) = 0 . \quad (17)$$

The Schrödinger equation in this form is actually not useful for numerical solutions of the reactive scattering problem, since the evaluation of the function $\mathcal{F}_{L'l'n';s}^{(\beta)}(N_\alpha, n_\alpha)$ requires a previous knowledge of the scattering solutions $F_{L'l'n'}^{(\beta)}(N_\beta)$. However, in the nontrivial case that the transferred particle 2 is very light, this equation can be solved approximately by making use of the results derived in this paper.

The great importance of transformations (15) and (16) will be illustrated now for several approaches taken to solve the quantum mechanical reactive scattering problem. As a first example of the use of these transformations, we consider the distorted wave Born

approximation in which the reaction amplitude for the transition $L, l, n \to L', l', n'$ is given by

$$T_{Lln,L'l'n'}^{J} = (X_{Lln}^{(1)(-)}(N_1)v_{nl}^{(1)}(n_1)\mathcal{Y}_{JM}(L, l; \hat{N}_1, \hat{n}_1) |$$
$$\times V | X_{L'l'n'}^{2(+)}(N_2)v_{n'l'}^{(2)}(n_2)\mathcal{Y}_{JM}(L', l'; \hat{N}_2, \hat{n}_2)) \ . \tag{18}$$

Here V is the interaction responsible for inelastic and reactive transitions; $X_{Lln}^{(1)(-)}(N_1)$ is the incoming elastic scattering solution in the entrance channel; $X_{L'l'n'}^{2(+)}(N_2)$ is the outgoing elastic scattering solution in the exit channel. If the potential is separated into radial and angular dependent factors as in (8), and transformations (15) and (16) are applied, the reaction amplitude reads

$$T_{Lln,L'l'n'}^{J} = \sum_{L'',l'',s,t} S_{angle}(L,l;L'',l'';s,t)(X_{Lln}^{(1)(-)}(N_1,n_1)v_{ln}^{(1)}(n_1) | V_s | \mathcal{F}_{L''l''n'';t}^{(2)}(N_1,n_1)_s C_{L'l';L''l''}^{J}(N_1,n_1)) \ . \tag{19}$$

The angular integral

$$S_{angle}(L,l;L'',l'';s,t) = (\mathcal{Y}_{JM}(L,l;\hat{N}_1,\hat{n}_1) | P_s(\cos\phi_2) | \mathcal{Y}_{JM}(L'',l'';\hat{N}_1,\hat{n}_1)\mathcal{Y}_{00}(t,t;\hat{N}_1,\hat{n}_1)) \tag{20}$$

can be expressed in terms of nj symbols, as is well known from the theory of inelastic scattering. However, in contrast to the angular momentum coupling for inelastic processes, the scattering amplitude for reactive collisions contains the additional radial dependent coupling coefficients $_sC_{L'l';L''l''}^{J}(N_1, n_1)$ which enter the translational–vibrational coupling term. The advantage of our procedure over the usual method[1] of integrating (18) numerically relies on the fact that our recoupling coefficients $_sC_{L'l';L''l''}^{J}(N_1, n_1)$ can be obtained in an analytical form. This means that the integration in (18) over rapidly oscillating angular wavefunctions (for angular momentum quantum numbers as high as encountered in molecular reaction processes) can be dealt with in an exact manner, and that one relies on a numerical integration procedure only to obtain the functions $\mathcal{F}_{L'l'n';t}^{(\beta)}(N_\alpha, n_\alpha)$.

To illustrate the significance of the recoupling coefficients $_sC_{L'l';L''l''}^{J}(N_2, n_2)$, let us consider a model reaction with a collision complex confined so that the translational–vibrational coupling terms in (19) are well localized, say around (N_0, n_0). In that case the radial integrals are proportional to $_sC_{L'l';L''l''}^{J}(N_0, n_0)$. The recoupling coefficients then establish selection rules for the reactive transitions in that one can predict that the dominant transitions have large values of the products

$$S_{angle}(L, l; L'', l''; s, t)_s C_{L'l';L''l''}^{J}(N_0, n_0) \ .$$

It will be seen later that the recoupling coefficients $_sC_{L'l';L''l''}^{J}(N_0, n_0)$ show a pronounced dependence on the masses of the colliding particles. It is therefore understandable that the final population of rotational states depends on the atomic masses of the reacting particles as well as on the geometry of the collision complex defined by N_0 and n_0.

A possible approach to treat reactive molecular collision processes in a more exact manner is as follows: Consider the Schrödinger equation reduced to a system of coupled two-dimensional differential equations em-

ploying only reactant basis functions

$$\sum_{L',l',n'} \int d\hat{N}_1 \int d\hat{n}_1 \mathcal{Y}_{JM}^*(L, l; \hat{N}_1, \hat{n}_1)(H - E)$$
$$\times \mathcal{Y}_{JM}(L', l'; \hat{N}_1, \hat{n}_1)F_{L'l'n'}^{(1)}(N_1)v_{n'l'}^{(1)}(n_1) = 0 \ . \tag{21}$$

This set of equations is integrated between the asymptotic region and the collision complex region, carrying two independent solutions for each channel. The N solutions (N being the number of reactant and product channels) are transformed in the collision complex region from the (N_1, n_1) coordinates to the (N_2, n_2) coordinates employing the transformation procedure above. The transformed wavefunction can then be matched to N independent solutions of the Schrödinger equation in the product coordinates:

$$\sum_{L',l',n'} \int d\hat{N}_2 \int d\hat{n}_2 \mathcal{Y}_{JM}^*(L, l; \hat{N}_2, \hat{n}_2)(H - E)$$
$$\times \mathcal{Y}_{JM}(L', l'; \hat{N}_2, \hat{n}_2)F_{L'l'n'}^{(2)}(N_2)v_{n'l'}^{(2)}(n_2) = 0 \ . \tag{22}$$

In this method the transformation procedure carrying the wavefunction from the (N_1, n_1) coordinates to the (N_2, n_2) coordinates provides for the necessary matching of reactant and product wavefunctions.

Another approach to solve the three-dimensional reactive scattering problem is to employ the Schrödinger equation in the (N_1, n_1) coordinates (21) throughout,[10] expanding

$$\mathcal{L} = \sum_{L',l',n'} F_{L'l'n'}^{(1)}(N_1)v_{n'l'}^{(1)}(n_1)\mathcal{Y}_{JM}(L', l'; \hat{N}_1, \hat{n}_1) \ . \tag{23}$$

The Schrödinger equation then has to be integrated along the vibrational coordinate n_1 out in the valley $N_2 \to \infty$ towards the asymptotic region of the reaction products. Since the partial waves in expansion (23) are not suitable to describe the asymptotic motion of the reaction products, the wavefunction has to be transformed to the product coordinates (N_2, n_2), finally. Again, the transformation procedure proposed will serve this task.

There exists yet another way to transform reactive scattering wavefunctions from reactant to product coordinates which has been proposed for nuclear reactive scattering.[11] One may separate from the radial part of the wavefunction (23) the factors N_1^L and n_1^l and expand the solid spherical harmonics

$$N_1^L n_1^l \mathcal{Y}_{JM}(L, l; \hat{N}_1, \hat{n}_1)$$

$$= \sum_{L', l'} {}_3 D_{Ll; L' l'}^J (N_2, n_2) \mathcal{Y}_{JM}(L', l'; \hat{N}_2, \hat{n}_2) \qquad (15')$$

and accordingly the remaining radial part

$$\frac{F_{Ll n}^{(1)}(N_1)}{N_1^L} \frac{v_{nl}^{(1)}(n_1)}{n_1^l} = \sum_s \mathcal{G}_{Ll n:s}^{(1)}(N_2, n_2) \mathcal{Y}_{00}(s, s; \hat{N}_2, \hat{n}_2) . \qquad (16')$$

This second set of expansions is very suggestive for actual calculations in that expansion (15') is finite and simpler to evaluate than the infinite expansion (15). However, difficulties appear now in the numerical evaluation of the functions $\mathcal{G}_{Ll n:s}^{(1)}(N_2, n_2)$. For large angular momentum quantum numbers L and l, the powers N_1^{-L} and n_1^{-l} in (16') are rapidly varying. Hence, the series $\mathcal{G}_{Ll n:s}^{(1)}(N_2, n_2)$ may be slowly convergent, as will be seen in Sec. V. One may say that the two sets of transformations (15), (16) and (15'), (16') are complementary in that the latter should be used for reactions that involve small angular momentum quantum numbers, while the first set should be used for reactions with large angular momentum quantum numbers.

III. REACTANT-PRODUCT TRANSFORMATION FOR TWO-DIMENSIONAL ANGULAR MOMENTUM STATES

To solve angular momentum coupling problems for three-dimensional motions, it is always instructive first to study the analogous problems for planar angular motion. All steps in the algebra of three-dimensional angular momentum coupling have their direct counterpart in the much simpler algebra of two-dimensional angular momentum coupling. This also holds true for the more complicated coupling of reactant and product angular momenta which will be derived in Sec. IV. Thus, we impose in this section the restriction that the colliding particles move in a *fixed* plane. The derivation of the equations, which describe the decomposition of reactant angular momentum states into product angular momentum states, is then particularly transparent and can be generalized to the three-dimensional case in a straightforward manner.

On the reactant and product side, the three-particle wavefunction must go asymptotically to

$$_\alpha = \sum_{m,n} F_{Mmn}^{(\alpha)}(N_\alpha) v_{nm}^{(\alpha)}(n_\alpha) \mathcal{Y}_M(m; \hat{N}_\alpha, \hat{n}_\alpha) \qquad \alpha = 1, 2, \qquad (24)$$

which differs from the three-dimensional wavefunction only in the total angular momentum states

$$\mathcal{Y}_M(m; \hat{N}_\alpha, \hat{n}_\alpha) = (1/2\pi) e^{i(M-m)\hat{N}_\alpha} e^{im\hat{n}_\alpha} . \qquad (25)$$

The total angular momentum quantum number M is the sum of the orbital angular momentum quantum number $M - m$ and the molecular rotational angular momentum quantum number m. The angles $\hat{N}_\alpha$ and $\hat{n}_\alpha$ define the directions of the position vectors N_α and n_α, respec-

tively.

The classical reactant orbital angular momentum $N_1 \times P_1$ and molecular rotational angular momentum $n_1 \times p_1$ are easily expressed in terms of product angular momenta by decomposing the position and momentum vectors into their product components by means of the transformation equations (2a) and (2b).[12] In quantum mechanics, rather than decomposing reactant vectors, one must decompose the corresponding state function depending on the reactant coordinates, into state functions depending on the product coordinates. Thus, the transformation of a free particle plane wave $e^{ir \cdot a}$ under a change of coordinates $a = \beta b + \gamma c$, which is analogous to either Eq. (2a) or Eq. (2b), is described by (see Fig. 2)

$$e^{ir \cdot a} = e^{i\beta r \cdot b} e^{i\gamma r \cdot c} . \qquad (26)$$

To extract the angular components of the free particle motion we expand each term in this equation in partial waves using[13]

$$e^{ir \cdot a} = \sum_n i^n J_n(pa) e^{in(\hat{a}-\hat{r})} \qquad (27)$$

and exploit the orthogonality property of $e^{in\hat{r}}$ to obtain

$$J_m(pa) e^{im(\hat{a}-\hat{b})} = \sum_{k=-\infty}^{+\infty} J_{m-k}(p\beta b) J_k(p\gamma c) e^{ik(\hat{c}-\hat{b})} . \qquad (28)$$

This equation is known as Graf's addition theorem,[13] and it holds for the whole family of similar triangles defined by $pa = p\beta b + p\gamma c$ for any positive p. We will average Eq. (28) over all similar triangles by integrating over dp/p, which of course leaves the angular functions unchanged. The weighting function $1/p$ is necessary to make the integral on the left side independent of a and the integral on the right depend on $\gamma c/\beta b$ only. After changing the order of summation and integration, we get

$$\int_0^\infty \frac{dx}{x} J_m(x) e^{im(\hat{a}-\hat{b})}$$

$$= (\text{sgn}\beta)^m \sum_k e^{ik(\hat{c}-\hat{b})} \int_0^\infty \frac{dy}{y} J_{m-k}(y) J_k\left(\frac{\gamma c}{\beta b} y\right) . \qquad (29)$$

By virtue of[13]

$$\int_0^\infty \frac{dx}{x} J_m(x) = \frac{1}{m} \qquad m > 0 , \qquad (30)$$

Eq. (29) may be rewritten

$$e^{im\hat{a}} = (\text{sgn}\beta)^m \sum_{k=-\infty}^{+\infty} F_k^m\left(\frac{\gamma c}{\beta b}\right) e^{i(m-k)\hat{b}} e^{ik\hat{c}} , \qquad (31)$$

where the expansion coefficients are defined by

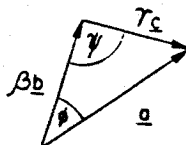$$F_k^m(x) = \int_0^\infty dy \frac{m}{y} J_{m-k}(y) J_k(xy) . \qquad (32)$$

FIG. 2. Definition of angles c and ψ.

This definition holds for the case $m > 0$. For $m < 0$, a factor $(-1)^m$ has to be included on the right side of Eq. (32). The integral in Eq. (32) is of the Weber–Schafheitlin type and can be evaluated analytically.[13] One finds for the case $m > 0$, $k \geq 0$, and $|x| \leq 1$,

$$F_k^m(x) = \binom{m/2}{k} x^k {}_2F_1\left(\frac{m}{2}, k - \frac{m}{2}; k+1; x^2\right) . \tag{33}$$

$\binom{m/2}{k}$ denotes the generalized binomial coefficient

$$\binom{m/2}{k} = \Gamma(1 + \tfrac{1}{2}m)/\Gamma(1+k)\Gamma(1 + \tfrac{1}{2}m - k) ,$$

and ${}_2F_1(a, b; a+b+1; x^2)$ stands for the hypergeometric function. The symmetry properties to be derived for the $F_k^m(x)$ allow one also to apply formula (32) to the remaining cases, $k \leq 0$, etc., as will be seen below. It might be noted that the case $m = 0$ is trivial,

$$F_k^0(x) = \delta_{0k} . \tag{34}$$

Equation (31) together with Eq. (33) constitutes the main result in the course of deriving the coupling algebra for two-dimensional reactant–product angular momentum states. Equation (31) has to be looked upon as a new addition theorem for the rotational wavefunctions $e^{im\hat{a}}$. The functions $e^{im\hat{a}}$ are the elements of the matrices forming the representation of the two-dimensional rotation group. The partial waves $J_m(pa) e^{im\hat{a}}$, however, are the elements of the matrix operators forming the representation of the Euclidean group. Noting that the rotational wavefunctions can be embedded in the representation of the Euclidean group

$$e^{im\hat{a}} = m \int_0^\infty \frac{dp}{p} J_m(pa) e^{im\hat{a}} , \tag{35}$$

the Euclidean group addition theorem for two-dimensional partial waves, Eq. (28), could be applied to yield a new addition theorem for two-dimensional rotational wavefunctions. This line of derivation can be applied in an obvious manner to derive a similar addition theorem for the three-dimensional spherical harmonics in Sec. IV.

We will now examine the functional properties of the expansion coefficients $F_k^m(x)$. From Eq. (32) follows immediately

$$F_k^m(x) = (-1)^k F_k^m(-x) . \tag{36}$$

Two symmetry properties can be easily derived. Comparing Eq. (31) with its conjugate complex shows

$$F_k^m(x) = F_{-k}^{-m}(x) . \tag{37}$$

On application of the symmetry property of Bessel functions, $J_k(x) = J_{-k}(-x)$, one obtains from Eq. (32)

$$F_k^m(x) = \frac{m}{m-2k} F_{-k}^{m-2k}(-x) . \tag{38}$$

Interchanging the order of Bessel functions under the integral in Eq. (32) and rescaling the integration variable results in

$$F_k^m(x) = (\operatorname{sgn} x)^m F_{m-k}^m(x^{-1}) . \tag{39}$$

Because of these symmetry properties, one can always relate $F_k^m(x)$ to a $F_{k'}^{m'}(x')$ with $m' \geq 0$, $k' \geq 0$, and $|x'| \leq 1$.

Hence, the formula Eq. (33) is sufficient to evaluate $F_k^m(x)$ in every case.

There exist two important sum rules for the $F_k^m(x)$. Multiplying Eq. (31) by its conjugate complex and reordering the summation on the right results in the following orthogonality property:

$$\sum_{k=-\infty}^{+\infty} F_k^m(x) F_{k+s}^m(x) = \delta_{s0} . \tag{40}$$

In the collinear limit (all angles zero), (31) reduces to

$$\sum_{k=-\infty}^{+\infty} F_k^m(x) = 1 . \tag{41}$$

From Eq. (31) a generating function can be obtained for the $F_k^m(x)$ by noting that for $a = \beta b + \gamma c$

$$e^{im(\hat{a}-\hat{b})} = N\left[\frac{x_1 + x_2 z}{x_1 + x_2/z}\right]^{m/2} , \tag{42}$$

where $x_1 = \beta b$, $x_2 = \gamma c$, $z = e^{i(\hat{c}-\hat{b})}$, and

$$N = (\operatorname{sgn} x_1)^m \quad \text{for } |x_1| > |x_2| ,$$
$$N = (\operatorname{sgn} x_2)^m \quad \text{for } |x_2| > |x_1| .$$

Comparing (42) with (31) thus gives

$$\left[\frac{1+xz}{1+x/z}\right]^{m/2} = \sum_{k=-\infty}^{\infty} F_k^m(x) z^k \qquad |x| \leq 1 . \tag{43}$$

This result could be derived directly using the definition of hypergeometric functions. For $x = 1$, (43) goes over to

$$z^{m/2} = \sum_{k=-\infty}^{+\infty} F_k^m(1) z^k , \tag{44}$$

so that for m even

$$F_k^m(1) = \delta_{k, m/2} \tag{45a}$$

and for m odd

$$F_k^m(1) = \frac{\sin(\tfrac{1}{2}m - k)\pi}{\pi(\tfrac{1}{2}m - k)} . \tag{45b}$$

From the theory of hypergeometric functions, the recursion relationship

$$x(k - \tfrac{1}{2}m - 1) F_{k-1}^m(x)$$
$$= [k + (k-m)x^2] F_k^m(x) - x(k - \tfrac{1}{2}m + 1) F_{k+1}^m(x) \tag{46}$$

results.

A method to evaluate the series of functions $F_k^m(x)$ most efficiently is represented in Appendix A.

Now that the properties of the expansion coefficients $F_k^m(x)$ have been worked out, let us see how Eq. (31) can be applied to set up the reactant–product transformation for the total angular momentum wavefunction (25). The reactant orbital and molecular angular momentum states $e^{i(M-m)\hat{N}_1}$ and $e^{im\hat{n}_1}$, respectively, can be expressed in terms of product coordinates by use of Eq. (31) in connection with coordinate transformations (2a) and (2b):

$$e^{i(M-m)\hat{N}_1} = (-1)^{M-m} \sum_{k_1=-\infty}^{+\infty} F_{k_1}^{M-m}\left(-\frac{n_2}{N_2}\tan\beta\right) e^{i(M-m-k_1)\hat{N}_2} e^{ik_1\hat{n}_2} , \tag{47}$$

$$e^{im\hat{n}_1} = (-1)^m \sum_{k_2=-\infty}^{\infty} F_{k_2}^m \left(\frac{N_2}{n_2}\tan\beta\right) e^{i(m-k_2)\hat{n}_2} e^{ik_2\hat{n}_2} . \tag{48}$$

These equations multiplied together give the desired result:

$$\mathcal{Y}_M(m;\hat{N}_1,\hat{n}_1) = \sum_{m'} {}_2C_{mm'}^M(N_2,n_2)\mathcal{Y}_M(m';\hat{N}_2,\hat{n}_2) \tag{49}$$

with

$$_2C_{mm'}^M(N_2,n_2) = (-1)^M \sum_{k=-\infty}^{\infty} F_{k+m'-m}^{M-m}\left(-\frac{n_2}{N_2}\tan\beta\right) F_k^m\left(\frac{N_2}{n_2}\tan\beta\right) . \tag{50}$$

The explicit mass dependence of the arguments appearing in the F coefficients might be stated

$$\frac{n_2}{N_2}\tan\beta = -\frac{r_2}{R_2}\frac{m_3(m_1+m_2+m_3)}{m_2(m_1+m_3)} , \tag{51a}$$

$$\frac{N_2}{n_2}\tan\beta = -\frac{R_2}{r_2}\frac{(m_1+m_3)}{m_1} . \tag{51b}$$

The transformation coefficients $_2C_{mm'}^M(N_2,n_2)$ show properties similar to those of the $F_k^m(x)$,

$$\sum_{m'} {}_2C_{mm'}^M(N_2,n_2) = (-1)^M , \tag{52}$$

$$\sum_{m'} {}_2C_{mm'}^M(N_2,n_2)\,{}_2C_{m,m'+s}^M(N_2,n_2) = \delta_{s,0} . \tag{53}$$

Formula (49) together with (50) allows one to express the reactant total angular momentum wavefunction in terms of product total angular momentum wavefunctions. This result can be applied directly in reactive scattering calculations as shown in Sec. II. Transformation (49) conserves total angular momentum and, hence, total parity.

It has been pointed out in Sec. II that for collisions with small angular momentum quantum numbers, one should employ solid spherical harmonics rather than spherical harmonics to transform from reactant to product states. Hence, we will derive now a transformation formula for two-dimensional solid harmonics.

The addition theorem for two-dimensional solid harmonics $a^m e^{im\hat{a}}$ is the binomial expansion of $ae^{i\hat{a}} = be^{i\hat{b}} + ce^{i\hat{c}}$ and may be written, for $m > 0$, as

$$a^m e^{im\hat{a}} = (\beta b)^m \sum_{k=0}^{m} G_k^m\left(\frac{\gamma c}{\beta b}\right) e^{i(m-k)\hat{b}} e^{ik\hat{c}} , \tag{54}$$

where

$$G_k^m(x) = \binom{m}{k} x^k \qquad \text{for } m \geq 0 . \tag{55}$$

The $G_k^m(x)$ coefficients exhibit the same symmetries as the coefficients $F_k^m(x)$:

$$G_k^m(x) = G_{-k}^{-m}(x) , \tag{56}$$

$$G_k^m(x) = G_{m-k}^m(x^{-1}) . \tag{57}$$

In the following we will define $\binom{m}{k}$ in Eq. (55) to be the generalized binomial coefficients so that we can extend in Eq. (54) the summation formally over all integer k. Applying Eq. (54) to the coordinate transformation (2a), (2b) then gives

$$N^{|M-m|}n_1^{|m|}\mathcal{Y}_M(m;\hat{N}_1,\hat{n}_1) = [(\cos\beta)N_2]^{|M-m|}[(\cos\beta)n_2]^{|m|}$$
$$\times \sum_{m'} D_{mm'}^M(N_2,n_2)\mathcal{Y}_M(m';\hat{N}_2,\hat{n}_2) \tag{58}$$

with

$$D_{mm'}^M(N_2,n_2) = \sum_k G_{k+m_2-m_1}^{M-m}\left(-\frac{n_2}{N_2}\tan\beta\right) G_k^m\left(\frac{N_2}{n_2}\tan\beta\right) . \tag{59}$$

Let us now compare the series of coefficients $F_k^m(x)$ and $G_k^m(x)$: For small x the $F_k^m(x)$ are centered around $k = 0$ $[F_k^m(0) = \delta_{k0}]$. As x increases the $F_k^m(x)$ spread out over the range $-\infty < k \leq \frac{1}{2}m$ and are slowly convergent in the immediate neighborhood of $x = 1$. However, for even m, $F_k^m(1)$ is completely localized at $k = m/2$ $[F_k^m(1) = \delta_{km/2}]$. The series $F_k^m(x^{-1})$ is the mirror image of $F_k^m(x)$ with respect to $k = m/2$, as follows from Eq. (39). Hence, for $x > 1$ the series $F_k^m(x)$ shifts abruptly over to the range $\frac{1}{2}m \leq k < \infty$. For large x, the $F_k^m(x)$ are confined around $k = m$. In Fig. 3 the series $F_k^{10}(x)$ and $F_k^{10}(x^{-1})$ are represented for $x = 0.52$.

The functional behavior of the series $G_k^m(x)$ is quite different. First, this series is not normalized, so that the values of $G_k^m(x)$ can exceed ± 1 by orders of magnitude, whereas the $F_k^m(x)$ vary between ± 1 only. Second, the series $G_k^m(x)$ is always confined within the finite range $0 \leq k \leq m$, peaking near $k = 0$ for small x and near $k = m$ for large x. In Fig. 3 the two series $G_k^{10}(x)$ and $G_k^{10}(x^{-1})$ are represented for $x = 0.52$. Note that the series $G_k^{10}(x)$ and $F_k^{10}(x)$ both assume their largest value for $k = 3$.

We will now present for some sample reactions the reactant–product angular momentum coupling coefficients $_2C_{mm'}^M$. Most of the calculations on molecular reactive collisions have dealt with the reaction $H + H_2 = H_2 + H$. In Fig. 4 we give the coupling coefficients $_2C_{2m'}^5$ of this reaction for the three atom configurations indicated ($R_2 = r_2$, $0 \leq \phi \leq 2\pi$) and assuming $M = 5$ as the total angular momentum quantum number and $m = 2$ as the reactant rotational quantum number. One observes that the coefficients peak around $m' = 2$, so that the coupling to a final rotational angular momentum state 2 appears to be strongest. However, the coupling coefficients spread over a wide range, so that coupling to product rotational states up to about $m' = 10$ seems to be
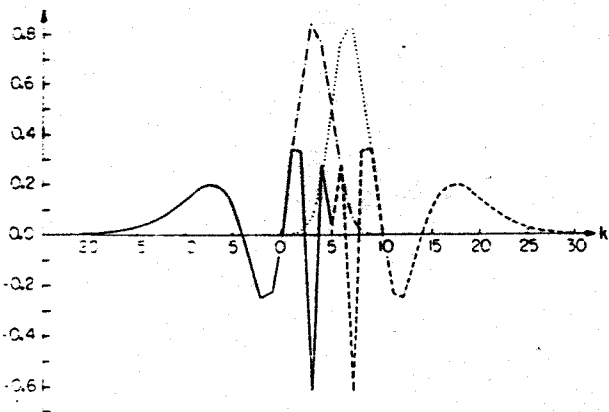
FIG. 4. Absolute values of $_2C_{2m'}^5$ for the reaction $H + H_2 = H_2 + H$ ($R_2 = r_2$, $0 \le \phi_2 \le 2\pi$).
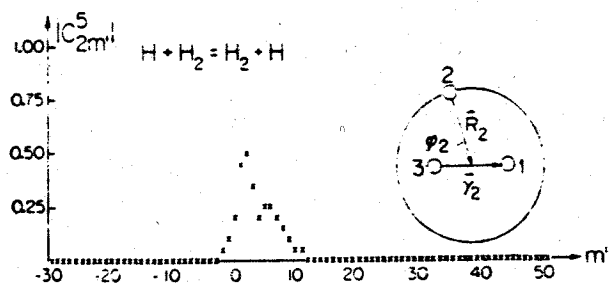

FIG. 6. Absolute values of $_2C_{2m'}^{40}$ for the reaction $K + HBr = KBr + H$ ($R_2 = 2.5r_2$, $0 \le \phi \le 2\pi$).

important. This is in agreement with quantum mechanical calculations on the planar H_3 system, where it has been found that closed rotational states have to be taken into account in order for the reactant–product transformation to be unitary.[1b] Figure 5 shows the same coupling coefficients for the reaction $H + D_2 = HD + D$ which are very similar to those coefficients for the H_3 system.

The reaction $K + HBr = KBr + H$ is known to occur via electron jump from K to Br which takes place at very large distances. The coupling coefficients for this reaction are given in Fig. 6 for the configuration ($R_2 = 2.5\,r_2$, $0 \le \phi \le 2\pi$) and the reactant angular momentum quantum numbers $M = 40$ and $m = 2$. One expects for this reaction that the reactant orbital angular momentum ($M - m = 38$) which involves mainly the relative motion of the K and Br atoms goes over to the product rotational angular momentum. This is indeed shown by the coefficients in Fig. 6, which indicate that the reactant angular momentum state $\mathcal{Y}_{40}(2; \hat{N}_1, \hat{n}_1)$ couples most strongly to the product angular momentum state $\mathcal{Y}_{40}(38; \hat{N}_2, \hat{n}_2)$, the coupling decaying rapidly for higher product rotational states.

In Fig. 7 we present coupling coefficients for the reaction $Cl + HBr = HCl + Br$ for the configuration ($R_2 = r_2$, $0 \le \phi \le 2\pi$) and for the reactant quantum numbers $M = 20$ and $m = 2$. In this case the reactant orbital angular momentum ($M - m = 18$) is expected to be carried into product orbital angular momentum. This is indeed reflected by the coupling coefficients which peak at $m' = 1$ so that the product orbital–angular momentum state $M - m' = 19$ is preferentially coupled to the reactant state. The coupling coefficients for the reaction $Li + HF = LiF + H$ are of interest because in this reaction
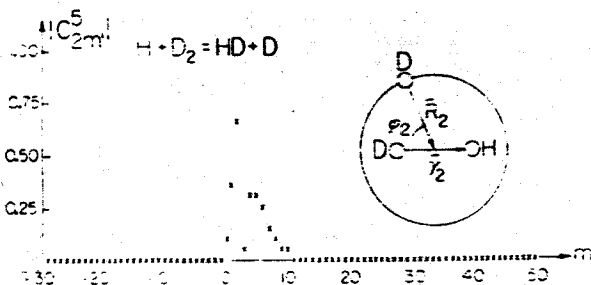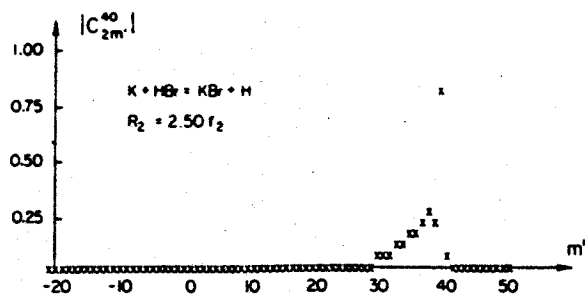
with a heavy transferred atom one expects that the reactant rotational angular momentum becomes product orbital angular momentum, and *vice versa*, the reactant orbital angular momentum goes into product rotational angular momentum.[14] The coupling coefficients in Fig. 8 evaluated for the configuration ($R_2 = r_2$, $0 \le \phi \le 2\pi$) and for the reactant angular momentum quantum numbers $M = 9$ and $m = 3$ reflect this exchange of angular momentum quantum numbers though there is a considerable spread over product rotational states m'.

A word should be said about the origin of the spread of product angular momentum values predicted by the reactant–product angular momentum transformation in Figs. 4–8. Comparison with the equivalent classical transformation shows that to a pair of reactant angular momentum quantum numbers (M, m) can be attributed *one* pair of product quantum numbers (M', m') for a *specific* value of the angle ϕ_2. Since the transformation derived assumes an average over all angles ϕ_2 ($0 \le \phi_2 \le 2\pi$), the product quantum numbers spread over a whole range of values (M', m'). Hence, each section of the (M', m') distribution can be identified as originating from a "scattering" event connected with a certain relative orientation ϕ_2 of the colliding particles.[12]

IV. REACTANT–PRODUCT TRANSFORMATION FOR THREE-DIMENSIONAL ANGULAR MOMENTUM STATES

We are now going to derive the decomposition of reactant angular wavefunctions into product angular wavefunctions for the case of three-dimensional collision processes. First we observe that Eq. (35), relating angular wavefunctions and partial waves, can be generalized to the three-dimensional case,
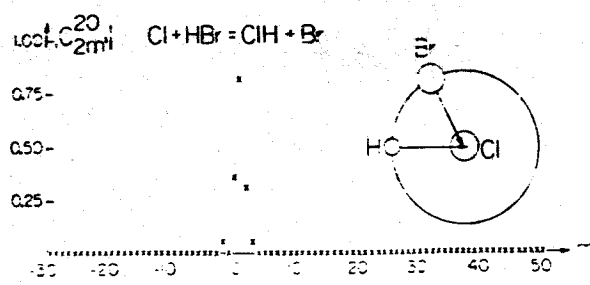

FIG. 5. Absolute values of $_2C_{2m'}^5$ for the reaction $H + D_2 = HD - D$ ($R_2 = r_2$, $0 \le \phi_2 \le 2\pi$).

FIG. 7. Absolute values of $_2C_{2m'}^{20}$ for the reaction $Cl + HBr = ClH + Br$ ($R_2 = r_2$, $0 \le \phi_2 \le 2\pi$).

$$Y_{lm}(\hat{a}) = \frac{4}{\sqrt{\pi}} \frac{\Gamma[(l+3)/2]}{\Gamma(\frac{l}{2})} \int_0^\infty \frac{dp}{p} j_l(pa) Y_{lm}(\hat{a}) . \tag{60}$$

Hence, the three-dimensional spherical harmonics $Y_{lm}(\hat{a})$ can be embedded in the representation of the three-dimensional Euclidean group given by the spherical waves $j_l(pa) Y_{lm}(\hat{a})$. For these spherical waves, again, an addition theorem can be derived. Starting from the vector addition $a = \beta b + \gamma c$ or from its quantum mechanical equivalent,

$$j_l(pa) Y_{lm}(\hat{a}) = \sqrt{4\pi} \sum_{l',l''} [(2l'+1)(2l''+1)]^{1/2} (-1)^{(l+l'+l'')/2} \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} j_{l'}(p\beta b) j_{l''}(p\gamma c) \mathcal{Y}_{lm}(l',l''; \hat{b},\hat{c}) . \tag{62}$$

This equation closely resembles the two-dimensional addition theorem (29), except for the coefficients on the right, which appear in the course of the coupling of three-dimensional angular momentum states. We suggest as an exercise to the reader to compare in detail the derivations of Eq. (29) and Eq. (62) to observe that any algebraic manipulation of the exponentials of the two-dimensional angular momentum states corresponds to the coupling of three-dimensional angular momentum states (summation over Clebsch–Gordan coefficients). As in the two-dimensional case, the addition theorem (62) together with Eq. (60) can be applied to yield a new addition theorem for spherical harmonics. This addition theorem will allow us to derive the formulas for the coupling of three-dimensional reactant–product angular momentum states.

Again, Eq. (62) holds for the whole family of similar triangles given by $pa = p\beta b + p\gamma c$ for any positive p. With the help of Eq. (60), the radial dependence can be averaged out by integrating (62) over dp/p to get the desired addition theorem

$$Y_{lm}(\hat{a}) = \sqrt{4\pi} (\text{sgn}\beta)^l \sum_{l',l''} F_{l'l''}^l \left(\frac{\gamma c}{\beta b}\right) \mathcal{Y}_{lm}(l',l''; \hat{b},\hat{c}) . \tag{63}$$

The expansion coefficients are defined by

$$F_{l'l''}^l(x) = \frac{4}{\sqrt{\pi}} (-1)^{(l+l'+l'')/2} \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} [(2l'+1)(2l''+1)]^{1/2}$$

$$\times \frac{\Gamma[(l+3)/2]}{\Gamma(l/2)} \int_0^\infty \frac{dy}{y} j_l(y) j_{l'}(xy) . \tag{64}$$

This is, for $|x| < 1$,[13]

$$F_{l'l''}^l(x) = \frac{\sqrt{\pi}}{2} [(2l'+1)(2l''+1)]^{1/2} (-1)^{(l+l'+l'')/2} \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \frac{\Gamma[(l+3)/2]}{\Gamma(l/2)} \frac{\Gamma[(l'+l'')/2]}{\Gamma(l''+\frac{3}{2}) \Gamma[(l'-l''+3)/2]} x^{l''}$$

$$\times {}_2F_1\left(\frac{l'+l''}{2}, \frac{l''-l'-1}{2}; l''+\frac{3}{2}; x^2\right) . \tag{65}$$

Equation (63) may be simplified by a transformation that aligns $\hat{b}$ with the z axis and rotates the triangle $a = \beta b + \gamma c$ into the x–z plane. By virtue of

$$\sum_{m'} \mathcal{Y}_{lm'}(l',l''; \hat{b},\hat{c}) D_{m'm}^l(\phi_{\hat{b}}, \theta_{\hat{b}}, \omega)$$

$$= \left[\frac{2l'+1}{4\pi}\right]^{1/2} (l'0l''m \mid lm) Y_{l''m}(\vartheta, 0) , \tag{66}$$

$$e^{i\gamma \cdot a} = e^{i\beta r \cdot b} e^{i\gamma r \cdot c} ,$$

we expand each term in this equation in partial waves according to[13]

$$e^{i\gamma \cdot a} = 4\pi \sum_{l,m} i^l j_l(pa) Y_{lm}(\hat{a}) Y_{lm}^*(\hat{p}) . \tag{61}$$

Then, making use of the orthogonality properties of the $Y_{lm}(\hat{p})$, we obtain after some calculation[15a]

where the rotation matrix elements $D_{m'm}^l$ are defined as in Rose,[16] and $\omega = \phi_{\hat{c}} - \phi_{\hat{b}}$, we get

$$Y_{lm}(\phi, 0) = (\text{sgn}\beta)^l \sum_{l',l''} (2l'+1)^{1/2} (l'0l''m \mid lm)$$

$$\times F_{l'l''}^l\left(\frac{\gamma c}{\beta b}\right) Y_{l''m}(\vartheta, 0) . \tag{67}$$

The angles ϕ and ϑ are defined in Fig. 2.

Equation (63), the three-dimensional counterpart of Eq. (31) in the previous section, will provide the basis for the recoupling of reaction complex angular momentum states. These equations together with the coordinate transformation (2a), (2b) can be directly applied to express reactant angular momentum states in terms of product angular momentum states.

Before we proceed, let us examine the properties of the expansion coefficients $F_{l'l''}^l(x)$. It should first be pointed out that the $F_{l'l''}^l(x)$ do not depend on magnetic quantum numbers. The reason for this can be seen from Eq. (67), which shows that the addition theorem relates only functions depending on the internal variables of the triangle $a = \beta b + \gamma c$, namely, the angles ϕ, ϑ and the ratio of the two sides $\gamma c / \beta b$. Since these variables are independent of the orientation of the triangle in a space fixed coordinate system, the expansion coefficients $F_{l'l''}^l(x)$ in (67) cannot depend on the magnetic quantum number m.

Two symmetry properties can be derived from Eq. (64). One can see immediately

$$F_{l'l''}^l(x) = (-1)^{l''} F_{l'l''}^l(-x) . \tag{68}$$
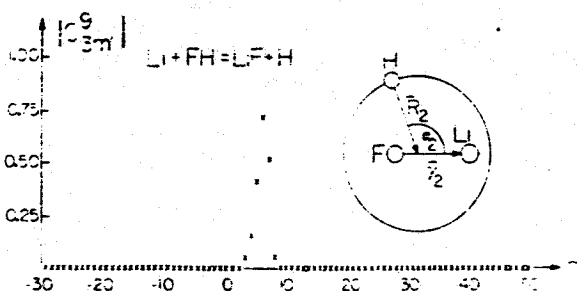
Changing the order of Bessel functions under the inte-

FIG. 8. Absolute values of ${}_2C_{3m'}^3$ for the reaction Li – FH = LiF + H ($R_2 = r_2$, $0 \le \phi_2 \le 2\pi$).

gral in (64) and rescaling the integration variable gives

$$F^l_{l'\,l''}(x) = (\text{sgn}\,x)^l F^l_{l'\cdot l''}(x^{-1}) . \tag{69}$$

Thus, we need to evaluate (64) for $|x| \le 1$ only.

There exist two useful sum rules. In the collinear limit, Eq. (67) reads

$$\sum_{l'\,l''} [(2l'+1)(2l''+1)]^{1/2} F^l_{l'\,l''}(|x|) \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} = (-1)^l . \tag{70}$$

In Appendix B we derive the orthogonality properties

$$\sum_{\substack{l'\,l'' \\ L'\,L''}} \begin{pmatrix} l' & L' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'' & L'' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L' & l' & \lambda \\ l'' & L'' & l \end{Bmatrix}$$

$$\times [(2l'+1)(2l''+1)]^{1/2} F^l_{l'\,l''}(x)$$

$$\times [(2L'+1)(2L''+1)]^{1/2} F^l_{L'\,L''}(x) = \delta_{\lambda 0} , \tag{71}$$

which in the case $\lambda = 0$ reduce to

$$\sum_{l'\,l''} [F^l_{l'\,l''}(x)]^2 = 1 . \tag{71'}$$

For the purpose of practical applications of Eq. (63), let us specify the summation over l' and l'' in more detail. The parity coefficients appearing in Eq. (65) make the $F^l_{l'\,l''}(x)$ vanish unless $l+l'+l''$ is even and $|l-l'| \le l'' \le l+l'$. We might therefore change the summation indices in (63):

$$Y_{lm}(\hat{a}) = \sqrt{4\pi} [\text{sgn}\beta]^l \sum_{i=0}^{l} \sum_{n=0}^{\infty} F^l_{l-i+n,\,i+n} \left(\frac{\gamma c}{\beta b}\right)$$

$$\times \mathcal{Y}_{lm}(l-i+n, \, i+n; \, \hat{b}, \, \hat{c}) . \tag{63'}$$

In Appendix A we show that the series of functions $F^l_{l-i+n,\,i+n}(x)$, $n = 0, 1, 2, \cdots$ can be generated easily by recursion.

We will now set up the transformation that connects reactant and product total angular momentum wavefunctions. To do so, we first express the reactant orbital angular momentum state $Y_{Lm_L}(\hat{N}_1)$ and the reactant molecular angular momentum state $Y_{lm_l}(\hat{n}_1)$ in terms of reactant coordinates by use of Eq. (63) together with the reactant-product coordinate transformation (2a), (2b):

$$Y_{Lm_L}(\hat{N}_1) = \sqrt{4\pi}(-1)^L \sum_{L_1 L_2} F^L_{L_1 L_2}\left(-\frac{n_2}{N_2}\tan\beta\right)$$

$$\times \mathcal{Y}_{Lm_L}(L_1, L_2; \hat{N}_2, \hat{n}_2) , \tag{72a}$$

$$Y_{lm_l}(\hat{n}_1) = \sqrt{4\pi}(-1)^l \sum_{l_1 l_2} F^l_{l_2 l_1}\left(\frac{N_2}{n_2}\tan\beta\right)$$

$$\times \mathcal{Y}_{lm_l}(l_1, l_2; \hat{N}_2, \hat{n}_2) . \tag{72b}$$

Since the F coefficients which describe the radial dependence of the transformation do not depend on the magnetic quantum numbers, they do not affect the coupling of angular momentum states. By virtue of

$$\sum_{m_L m_l} (Lm_L lm_l | JM) \mathcal{Y}_{Lm_L}(L_1, L_2; \hat{N}_2, \hat{n}_2) \mathcal{Y}_{lm_l}(l_1, l_2; \hat{N}_2, \hat{n}_2)$$

$$= \frac{1}{4\pi}(-1)^{L_1 \cdot L_2 \cdot l_1 \cdot l_2} \sum_{l', L'} \begin{pmatrix} L_1 & l_1 & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_2 & l_2 & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & l & J \\ L_1 & l_1 & L' \\ L_2 & l_2 & l' \end{Bmatrix} [(2L+1)(2L_1+1)(2L_2+1)(2L'+1)(2l+1)$$

$$\times (2l_1+1)(2l_2+1)(2l'+1)]^{1/2} \mathcal{Y}_{JM}(L', l'; \hat{N}_2, \hat{n}_2) , \tag{73}$$

we get the final formula

$$\mathcal{Y}_{JM}(L, l; \hat{N}_1, \hat{n}_1) = \sum_{L', l'} {}_3 C^J_{Ll;L'l'}(N_2, n_2) \mathcal{Y}_{JM}(L', l'; \hat{N}_2, \hat{n}_2) , \tag{74}$$

where the expansion coefficients are

$${}_3 C^J_{Ll;L'l'}(N_2, n_2) = \sum_{\substack{L_1, L_2 \\ l_1, l_2}} [(2L+1)(2L_1+1)(2L_2+1)(2L'+1)(2l+1)(2l_1+1)(2l_2+1)(2l'+1)]^{1/2}$$

$$\times \begin{Bmatrix} L & l & J \\ L_1 & l_1 & L' \\ L_2 & l_2 & l' \end{Bmatrix} \begin{pmatrix} L_1 & l_1 & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_2 & l_2 & l' \\ 0 & 0 & 0 \end{pmatrix} F^L_{L_1 L_2}\left(-\frac{n_2}{N_2}\tan\beta\right) F^l_{l_2 l_1}\left(\frac{N_2}{n_2}\tan\beta\right) . \tag{75}$$

Note that these transformation coefficients connect only total angular momentum states of the same total parity $(-1)^L(-1)^l = (-1)^{L'}(-1)^{l''}$. However, they allow for a change of the partial parities of orbital and rotational angular momentum which are not separately conserved.

Formula (74) together with (75) allows one now, for the case of three-dimensional collisions, to express reactant total angular momentum states in terms of product total angular momentum states or *vice versa*. This result can be applied directly to reactive scatter-

ing calculations, as shown in Sec. II.

The coefficients ${}_3 C^J_{Ll;L'l'}$ obey two sets of sum rules equivalent to the sum rules (70) and (71) for the $F^l_{l'\,l''}(x)$. We first observe that in the collinear limit, i.e., all angles being zero,

$$\mathcal{Y}_{JM}(L, l) = \frac{(-1)^J}{4\pi} [(2J+1)(2L+1)(2l+1)]^{1/2} \begin{pmatrix} L & l & J \\ 0 & 0 & 0 \end{pmatrix} \delta_{M0} . \tag{76}$$

Equation (74) reads then

$$\sum_{L',l'} [(2L'+1)(2l'+1)]^{1/2} \begin{pmatrix} L' & l' & J \\ 0 & 0 & 0 \end{pmatrix} {}_3C^J_{Ll:L'l'}(N_2,n_2)$$

$$= [(2L+1)(2l+1)]^{1/2} \begin{pmatrix} L & l & J \\ 0 & 0 & 0 \end{pmatrix} . \tag{77}$$

The orthogonality properties of the ${}_3C^J_{Ll:L'l'}(N_2,n_2)$ derived in Appendix B are given by

$$\sum_J \sum_{L'',l'' \atop L''',l'''} (-1)^J [(2L'+1)(2L''+1)(2l'+1)(2l''+1)]^{1/2}$$

$$\times \begin{pmatrix} L' & L'' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l'' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l'' & l' & \lambda \\ L' & L'' & J \end{Bmatrix} {}_3C^J_{Ll:L'l'}(N_2,n_2)$$

$$\times {}_3C^J_{Ll:L''l''}(N_2,n_2) = (2L+1)(2l+1)\delta_{\lambda 0} . \tag{78}$$

In the case that $\lambda=0$, this is

$$\sum_J \sum_{L',l'} (2J+1)[{}_3C^J_{Ll,L'l'}(N_2,n_2)]^2 = (2L+1)(2l+1) . \tag{78'}$$

These sum rules provide a very useful means to check the accuracy of any evaluation of the transformation coefficients.

We pointed out in Sec. II that the angular momentum transformation now derived gives to zeroth order the probability amplitude for the reactive transitions. For mathematical convenience the transformation has been derived in the total angular momentum basis. In the basis (Lm_L, lm_l), the transformation is

$$T_{Lm_L lm_l:L'm'_L l'm'_l}(N_2,n_2)$$

$$= \sum_J (Lm_L lm_l|JM) {}_3C^J_{Ll,L'l'}(N_2,n_2)(JM|L'm'_L l'm'_l) . \tag{79}$$

Hence, this expression gives the probability amplitude for the transition $(Lm_L, lm_l) \to (L'm'_L l'm'_l)$ and allows the study of the polarization of the final angular momentum states of the reaction products. If we are interested in the transitions $(L,l) \to (L',l')$, we average over the magnetic quantum numbers m_L, m_l and sum over the final states $m_{L'}, m_{l'}$:

$$P_{Ll:L'l'}(N_2,n_2) = \frac{1}{(2L+1)(2l+1)} \sum_{m_L m_l \atop m'_L m'_l} (T_{Lm_L lm_l:L'm'_L l'm'_l})^2$$

$$= \sum_J \frac{(2J+1)}{(2L+1)(2l+1)} [{}_3C^J_{Ll:L'l'}(N_2,n_2)]^2 . \tag{80}$$

From Eq. (78'), one can observe that the sum of all probabilities is one. The probabilities defined in Eq. (80) are of course not obtainable from experimental observations which do not select orbital angular momentum states. Recognizing that the probabilities for reactive transitions depend on the reactant orbital angular momentum quantum number L, we may include a weighting function $\bar{i}(L)$ to define the probability for the transition $l \to l'$,

$$P_{l,l'} = \sum_{L,L'} \bar{i}(L) P_{Ll:L'l'} .$$

In Sec. V we will evaluate zeroth order transition probabilities for some sample chemical reactions.

For systems that allow only small angular momentum values to occur in reactive collision processes, the transformation can be based on the decomposition of three-dimensional solid spherical harmonics. This transformation can be deduced from an addition theorem which will be derived now.[15b] We start from the observation that $a^l Y_{lm}(\hat{a})$ is a homogeneous polynomial of degree l in the Cartesian coordinates a_1, a_2, and a_3 of a. By use of $a_i = \beta b_i + \gamma c_i$, we can replace the variables a_i to get a homogeneous polynomial of the same degree in the variables βb_i and γc_i. Since the functions $(\beta b)^{l'} Y_{l'm'}(\hat{b})$ and $(\gamma c)^{l''} Y_{l''m''}(\hat{c})$ form a complete basis for these polynomials, we can expand

$$a^l Y_{lm}(\hat{a}) = \sum_{\lambda,m',m''} a_\lambda (\beta b)^{l-\lambda} (\gamma c)^\lambda Y_{l-\lambda m'}(\hat{b}) Y_{\lambda m''}(\hat{c}) . \tag{81}$$

However, the left side of this equation transforms like an angular momentum state (l,m), and the right side has to do so as well, which is the case only for the linear combination

$$\mathcal{Y}_{lm}(l-\lambda, \lambda; \hat{b}, \hat{c}) = \sum_{m',m''} (l-\lambda m' \lambda m''|lm) Y_{l-\lambda,m'}(\hat{b}) Y_{\lambda m''}(\hat{c}).$$

Hence, we can write

$$a^l Y_{lm}(\hat{a}) = \sum_{\lambda=0}^l b_\lambda (\beta b)^{l-\lambda} (\gamma c)^\lambda \mathcal{Y}_{lm}(l-\lambda, \lambda; \hat{b}, \hat{c}) . \tag{82}$$

To obtain the coefficients b_λ, we note that this equation has to go over in the collinear limit to $a^l = (\beta b + \gamma c)^l$ and conclude after some calculation

$$a^l Y_{lm}(\hat{a}) = \sqrt{4\pi} (\beta b)^l \sum_{\lambda=0}^l G^l_\lambda \left(\frac{\gamma c}{\beta b}\right) \mathcal{Y}_{lm}(l-\lambda, \lambda; \hat{b}, \hat{c}) , \tag{83}$$

where

$$G^l_\lambda(x) = \frac{1}{\sqrt{2\lambda+1}} \begin{pmatrix} 2l+1 \\ 2\lambda \end{pmatrix}^{1/2} x^\lambda . \tag{84}$$

The finite expansion (82) is clearly simpler than the infinite expansion (63) and therefore seems more desirable to apply in calculations. However, as will be pointed out in Sec. VI, for large angular momentum quantum numbers, the simplification gained with expansion (82) gives rise to difficulties in transforming the translational–vibrational part of the scattering wavefunction. To obtain the reactant–product transformation for the total angular momentum state, we apply the addition formula (83) to the coordinate transformation (2a), (2b) to get from

$$N_1^L Y_{Lm_L}(\hat{N}_1) = \sqrt{4\pi} [(-\cos\beta)N_2]^L \sum_{L_1} G^L_{L_1}\left(-\frac{n_2}{N_2}\tan\beta\right)$$

$$\times \mathcal{Y}_{Lm_L}(L-L_1, L_1; \hat{N}_2, \hat{n}_2) \tag{85a}$$

and from

$$n_1^l Y_{lm_l}(\hat{n}_1) = \sqrt{4\pi} [(-\cos\beta)n_2]^l \sum_{l_1} G^l_{l_1}\left(\frac{N_2}{n_2}\tan\beta\right)$$

$$\times \mathcal{Y}_{lm_l}(l_1, l-l_1; \hat{N}_2, \hat{n}_2) \tag{85b}$$

the desired expansion

$$N_1^L n_1^l \mathcal{Y}_{JM}(L,l;\hat{N}_1,\hat{n}_1) = (-\cos\beta N_2)^L(-\cos\beta n_2)^l \sum_{L',l'} {}_3D^J_{L,l;L',l'}(N_1,n_1)\mathcal{Y}_{JM}(L',l';\hat{N}_2,\hat{n}_2) , \tag{86}$$

where

$$
{}_3D^J_{Ll;L'l'}(N_2,n_2) = (2J+1) \sum_{L_1,l_1}
\begin{pmatrix} L-L_1 & l-l_1 & L' \\ 0 & 0 & 0 \end{pmatrix}
\begin{pmatrix} L_1 & l_1 & l' \\ 0 & 0 & 0 \end{pmatrix}
[(2L+1)(2L_1+1)(2L-2L_1+1)(2L'+1)(2l+1)
$$

$$
\times (2l_1+1)(2l-2l_1+1)(2l'+1)]^{1/2}
\left\{ \begin{matrix} L & l & J \\ L-L_1 & l_1 & L' \\ L_1 & l-l_1 & l' \end{matrix} \right\}
G^L_{L'}\left(-\frac{n_2}{N_2}\tan\beta\right) G^l_{l_1}\left(\frac{N_2}{n_2}\tan\beta\right) . \tag{87}
$$

The conservation of total parity holds for this transformation too.

V. TRANSFER OF ANGULAR MOMENTUM IN SOME SPECIFIC REACTIONS

The usefulness of the reactant–product angular momentum coupling coefficients

$$
{}_3C^J_{Ll;L'l'}(N_2,n_2) = \langle \mathcal{Y}_{JM}(L,l;\hat{N}_1,\hat{n}_1) | \mathcal{Y}_{JM}(L',l';\hat{N}_2,\hat{n}_2) \rangle
$$

lies in their application as a calculational tool in the quantum mechanical theory of molecular reactions. The analytic representation of the ${}_3C^J_{Ll;L'l'}$ coefficients reduces the explicit evaluation of the more general matrix elements

$$
\langle \mathcal{Y}_{JM}(L,l;\hat{N}_1,\hat{n}_1) | P_\lambda(\cos\phi_2) | \mathcal{Y}_{JM}(L',l';\hat{N}_2,\hat{n}_2) \rangle
$$

to a problem of ordinary angular momentum coupling. This role of the coupling coefficients which motivated our work has been explained at length in Sec. II. It is possible, however, without engaging in a full scale reactive scattering calculation, to learn a great deal about the rotational motion in molecular reactions from the ${}_3C^J_{Ll;L'l'}$ coefficients alone.

The coupling coefficients in the ordinary theory of angular momentum coupling provide the quantum mechanical description for the addition of angular momentum vectors in classical mechanics. The reactant–product angular momentum coupling coefficients ${}_3C^J_{Ll;L'l'}$ similarly provide the quantum mechanical description of the decomposition of reactant angular momenta into product angular momenta. The decomposition of reactant rotation into product rotation is of course the basis for the transfer of rotational motion in molecular reactions. The actual rotational motion of reactants and products will, in general, be perturbed by nonspherical interactions, and thus by the release of exothermic energy into rotational degrees of freedom. Nevertheless, the reactant–product angular momentum coupling coefficients provide an interesting zeroth order description of rotational motion in molecular reactions. Hence, in this section we will discuss some "zeroth order" distributions of the product rotational states obtained from an explicit evaluation of the ${}_3C^J_{Ll;L'l'}$'s.

In Appendix D we derived the coupling coefficients for the limiting cases $\beta = \frac{1}{2}\pi$ (heavy atom transfer reaction $L_1 + HL_2 = L_1H + L_2$) and $\beta = 0$ (light atom transfer reaction $H_1 + LH_2 = H_1L + H_2$). For the first case one finds

$$
{}_3C^J_{Ll;L'l'} = (-)^{J+l}\delta_{Ll'}\delta_{lL'} ,
$$

i.e., the reactant *orbital* angular momentum goes over into product *rotational* angular momentum and the re-

actant *rotational* angular momentum goes over into product *orbital* angular momentum[14] (see also Figs. 9 and 10). In the second case one finds

$$
{}_3C^J_{Ll;L'l'}(N_2,n_2)
$$

$$
= (-1)^{J+L'} \sum_{l_1} [(2L+1)(2l+1)(2l_1+1)(2L'+1)]^{1/2}
$$

$$
\times \left\{ \begin{matrix} L' & l_1 & L \\ l & J & l' \end{matrix} \right\}
\begin{pmatrix} L & l_1 & L' \\ 0 & 0 & 0 \end{pmatrix}
F^l_{l'l_1}\left(-\frac{R_2}{r_2}\right) ,
$$

i.e., reactant *orbital* angular momentum contributes only to product *orbital* angular momentum, whereas the reactant *rotational* angular momentum contributes to both *orbital* and *rotational* angular momenta of the products.

The distributions of product rotational states are defined through

$$
A_{Ll;L'} = \sum_{J,l'} \frac{(2J+1)}{(2L+1)(2l+1)} |{}_3C^J_{Ll;L'l'}|^2
$$

(product orbital angular momentum distribution) and

$$
B_{Ll;l'} = \sum_{J,L'} \frac{(2J+1)}{(2L+1)(2l+1)} |{}_3C^J_{Ll;L'l'}|^2
$$

(product rotational angular momentum distribution). The summation over the total angular momentum quantum number J may be interpreted as the averaging over all relative orientations of the reactant angular momentum vectors L and l, since, for example, $|{}_3C^{L+l}_{Ll;L'l'}|^2$ gives the distribution of L' and l' for L and l being parallel, and $|{}_3C^{|L-l|}_{Ll;L'l'}|^2$ gives the distribution of L' and l' for L and l being antiparallel.

Figure 9(a) presents the product rotational distribution of the reaction Li + FH = LiF + H for $L=10$ (orbital angular momentum) and $l=3$ (rotational angular momentum). Since this reaction is of the type $L_1 + HL_2 = L_1H + L_2$, one expects an exchange of orbital and rotational angular momentum in the course of the reactive collision.[14] Indeed, the L' distribution is centered around $L' = 3$, while the l distribution is centered around $l' = 10$. An increase of the reactant rotational angular momentum from $l=3$ to $l=6$ does not shift the product rotational angular momenta, but broadens their distribution [Fig. 9(b)].

In evaluating product rotational distributions the value of r_2/R_2 may be chosen corresponding to a saddle point of the reaction potential surface. The value r_2/R_2 en-

ters the F coefficients in the expression for $_2C^l_{Ll;L'l'}$ (75) through the arguments as given by (51a) and (51b). In case of the reaction Li + FH = LiF + H, the arguments are $-(n_2/N_2)\tan\beta \approx 19.7(r_2/R_2)$ and $(n_2/N_2)\tan\beta \approx -3.7(R_2/r_2)$.
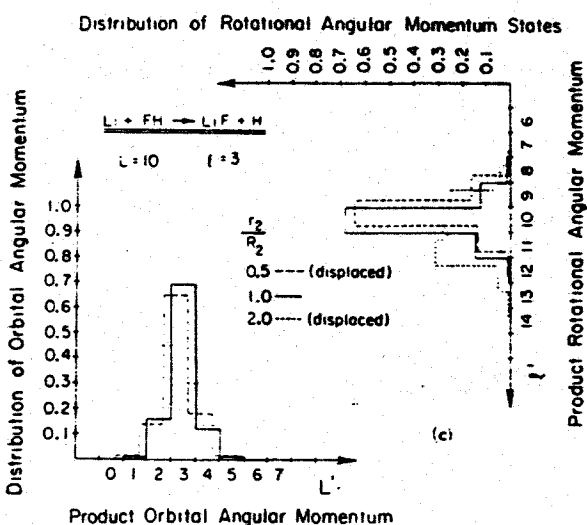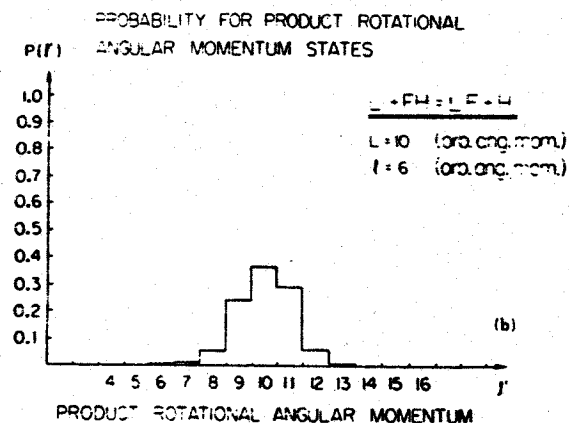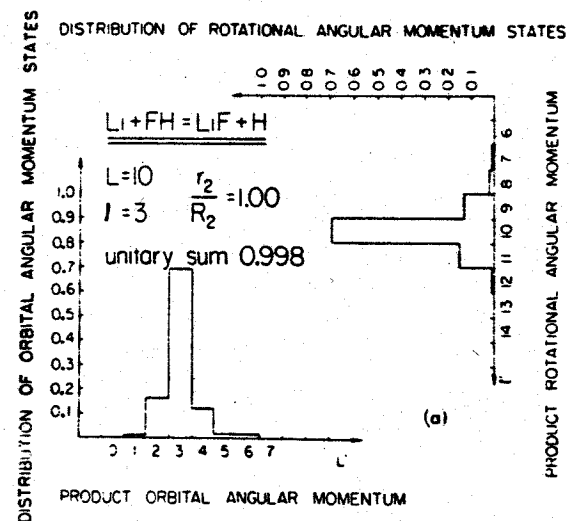

FIG. 9. (a) Distribution of product orbital and rotational angular momenta for Li + FH = LiF + H($L = 10$, $l = 3$, $r_2/R_2 = 1.0$). (b) Distribution of product rotational angular momenta for Li + FH = LiF + H($L = 10$, $l = 6$, $r_2/R_2 = 1.0$). (c) Comparison of product angular momentum distributions for Li + FH = LiF + H ($L = 10$, $l = 3$) with $r_2/R_2 = 0.5$, 1.0, and 2.0.
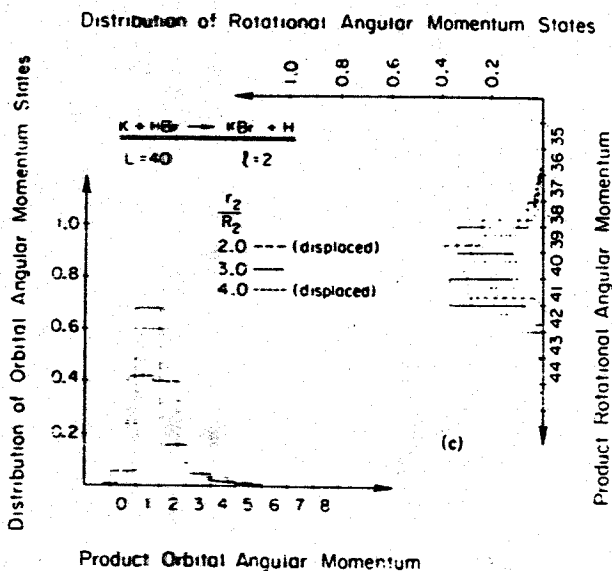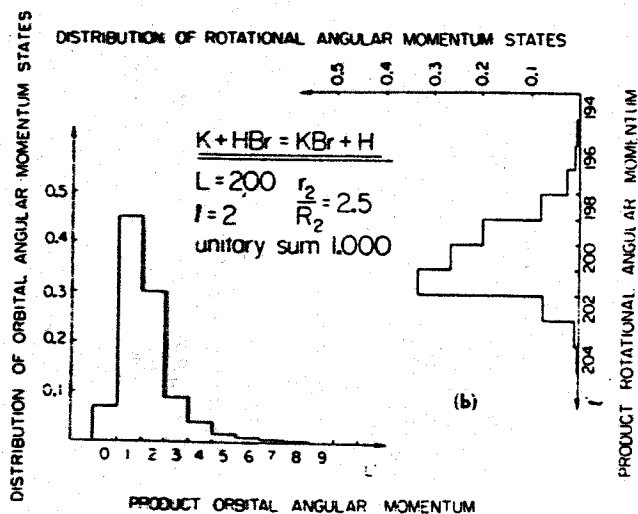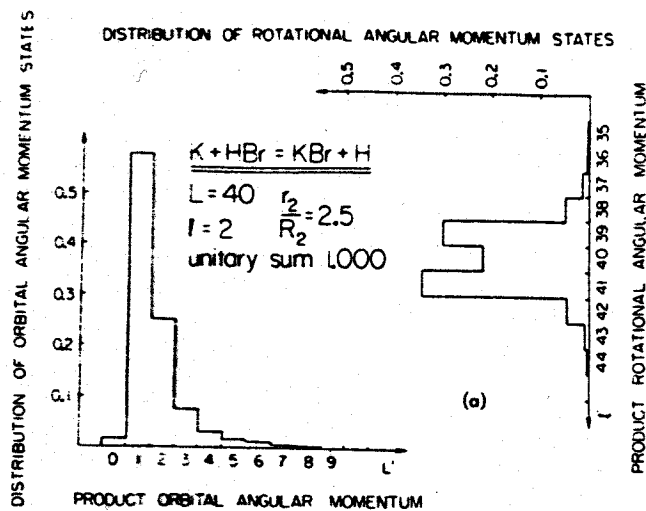
FIG. 10. (a) Distribution of product orbital and rotational angular momenta for K + HBr = KBr + H($L = 40$, $l = 2$, $r_2/R_2 = 2.5$). (b) Distribution of product orbital and rotational angular momenta for K + HBr = KBr + H($L = 200$, $l = 2$, $r_2/R_2 = 2.5$). (c) Comparison of product angular momentum distribution for K + HBr = KBr + H($L = 40$, $l = 2$) with $r_2/R_2 = 2.0$, 3.0 and 4.0.

Only if these arguments are close to 1.0 does the rotational distribution depend sensitively on the choice of r_2/R_2. To elucidate this we compare in Fig. 9(c) the rotational distribution for $r_2/R_2 = 0.5$, 1.0, and 2.0. In these cases the arguments of the F coefficients are $(9.87, -7.43)$, $(19.73, -3.71)$, and $(39.46, -1.86)$, respectively. The last argument is close to one, hence, the deviation of the $r_2/R_2 = 2.0$ distribution in Fig. 9(c).

As a second example we give the product rotational distributions for the reaction $K + HBr = KBr + H$. The distributions are similar to those of the previous reaction, i.e., they exhibit the typical exchange of orbital and rotational angular momenta in heavy atom transfer reactions.[14] The reaction has a large cross section[14] (~ 34 Å^2) and is therefore governed by large orbital angular momentum values ($\sim 100\hbar$). We chose this reaction to demonstrate that even such large angular momenta can be dealt with accurately. Figures 10(a) ($L = 40$, $l = 2$) and 10(b) ($L = 200$, $l = 2$) show the expected shift of the product rotational angular momentum from $l' \approx 40$ to $l' \approx 200$.

Let us illustrate again the dependence of the product rotational distribution on r_2/R_2. In Fig. 10(c) we compare distributions corresponding to r_2/R_2 values 2.0, 3.0, and 4.0. The arguments of the F coefficients are $(161.34, -1.53)$, $(242.02, -1.02)$, and $(322.69, -0.76)$. Since arguments for this reaction are close to 1.0, a stronger r_2/R_2 dependence of the product distribution is expected. This dependence, as can be seen from Fig. 10(c), smears out the fine structure of the distribution but does not change its average behavior.

Figure 11 shows the product angular momentum distributions for the reaction $Cl + HI = ClH + I$ with $L = 64$ and $l = 5$. For this light atom transfer reaction, one expects that *orbital* goes into *orbital* angular momentum and *rotational* goes into *rotational* angular momentum upon reaction. The product orbital angular momentum distribution is indeed centered around $L' = 64$. The product rotational angular momentum distribution is centered around $l' = 2$, which indicates a loss of rotational angular momentum ($\Delta l' = 3$-4) in favor of orbital motion. Hence, one finds the broadening of the L' distribution by $2\Delta l'$.

At this point it should be discussed how the zeroth order distributions $A_{Ll;L'}$ and $B_{Ll;l'}$ are related to the "exact" distributions which would come out of full scale calculations. Trajectory studies by Polanyi and co-workers[17] give, for the reaction $Cl + HI = ClH + I$ with $L = 64$ and $l = 5$, product distributions centered around $L' = 69$ and $l' = 14$. This indicates that in the course of this reaction (at least as far as the chosen potential surface is concerned) the repulsive release of energy between H and I leads to a high rotational excitation of the reaction products ($\Delta l' \approx 12$). For our calculations we have chosen two transition geometries, $r_2/R_2 = 0.55$ and $r_2/R_2 = 0.40$, corresponding in a collinear arrangement to transition points in the entrance and in the exit potential energy valley of Ref. 17. In comparing Figs. 11(a) and 11(b), one finds that the distributions are rather insensitive to the change of transition geometry. The zeroth order transition probabilities account for
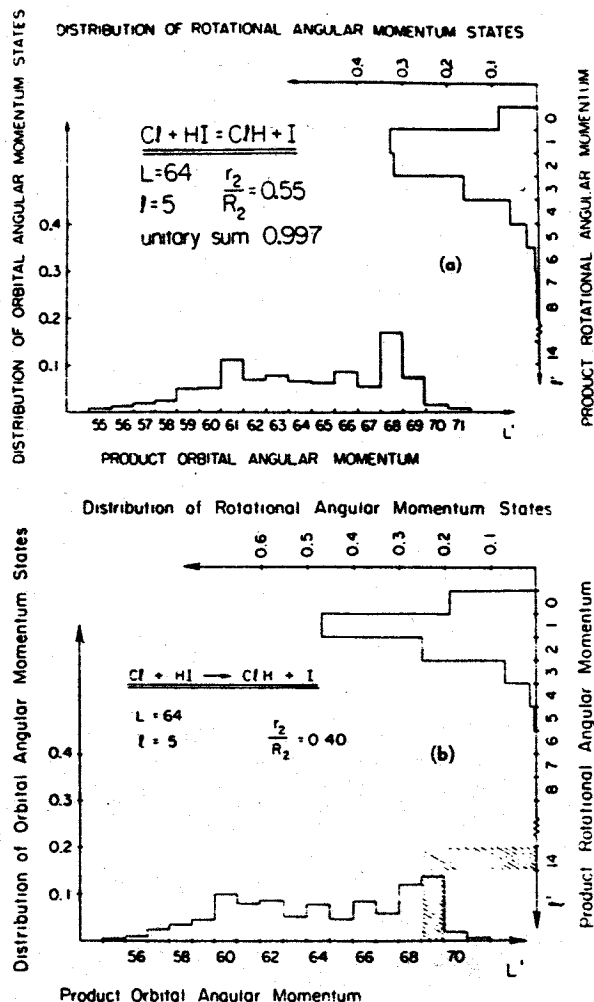

FIG. 11. Distribution of product orbital and rotational angular momenta for $Cl + HI = ClH + I$: (a) $L = 64$, $l = 5$, $r_2/R_2 = 0.55$; (b) $L = 64$, $l = 5$, $r_2/R_2 = 0.40$; trajectory results of Polanyi et al.,[17] shaded area.

neither the exothermicity of a reaction nor for the specific mechanism of the exothermic energy release, so that one has to expect in general that the zeroth order distributions are shifted to higher quantum numbers, the shift indicating the amount of reaction energy being stored in the rotational degrees of freedom. Further, one has to expect that the zeroth order distributions are broadened by nonspherical interactions in the reactant as well as in the product channels.

In the light of this discussion, the results presented in Fig. 12 for the reaction $H + Cl_2 = HCl + Cl$ with $L = 10$ and $l = 20$ are interesting. Polanyi et al.[17] have described this reaction on a potential surface identical to that of the previous $Cl + HI = ClH + I$ reaction, i.e., these authors just changed the masses of the reacting particles of this reaction. Hence, we have chosen for our calculation the same transition geometries as above, to which correspond r_2/R_2 values 0.8 and 0.5. The product orbital angular momentum L' distributions obtained both center around $L' = 20$, but the rotational angular momentum l' distributions are shifted from a peak at $l' = 8$ to $l' = 6$. A comparison with the classical trajec-
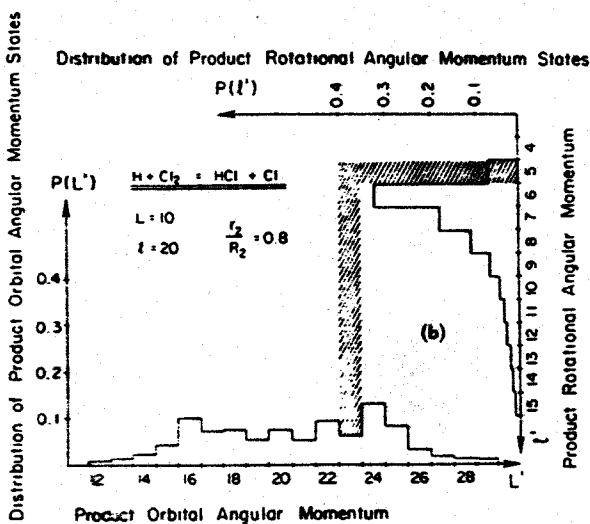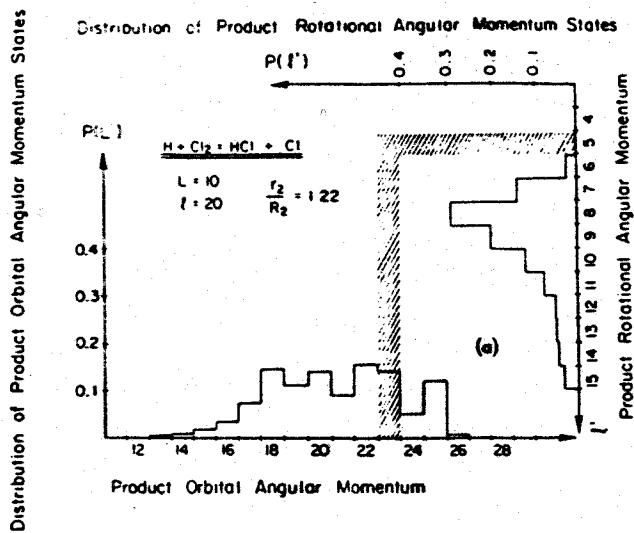
FIG. 12. Distribution of product orbital and rotational angular momenta for $H + Cl_2 = HCl + Cl$: (a) $L = 10$, $l = 20$, $r_2/R_2 = 1.22$; (b) $L = 10$, $l = 20$, $r_2/R_2 = 0.8$; trajectory results of Polanyi et al.,[17] shaded area.

tory results shows that for this mass combination there is no release of exothermic energy into the rotational degrees of freedom as in the reaction $Cl + HI = ClH + I$ proceeding on the same potential energy surface.

As a final example, in Figs. 13(a) and 13(b) we compare distributions for the reaction $F + D_2 = FD + D$ with classical trajectory results of Blais and Truhlar.[18a] For $L = 5$ and $l = 3$, the product distributions in Fig. 13(a) center around $L' = 5$ and $l' = 3$, where we assumed a r_2/R_2 value of 0.6 corresponding to the transition point on the potential energy surface of Ref. 18(a) with bond angle $F-D-D$ 180°. The trajectory results[18a] exhibit a shift to higher rotational states and a broadening of the distribution. This is also observed for the case of initial angular momenta $L = 10$ and $l = 3$ in Figs. 13(b) and 13(c). Here we have chosen r_2/R_2 values corresponding to the transition points of both the 180° and 100° $F-D-D$ bond angle potential surfaces.
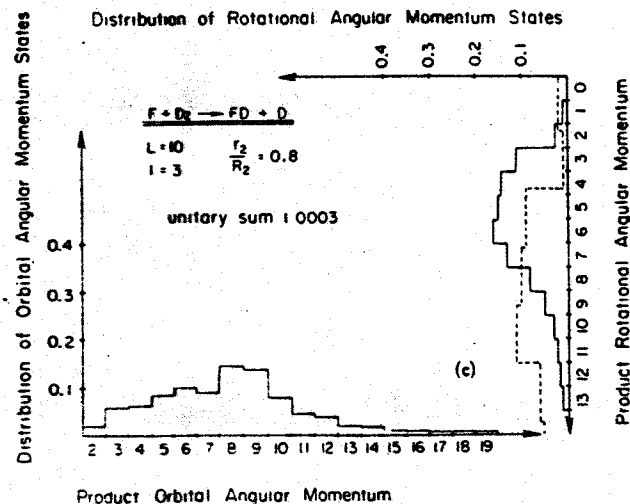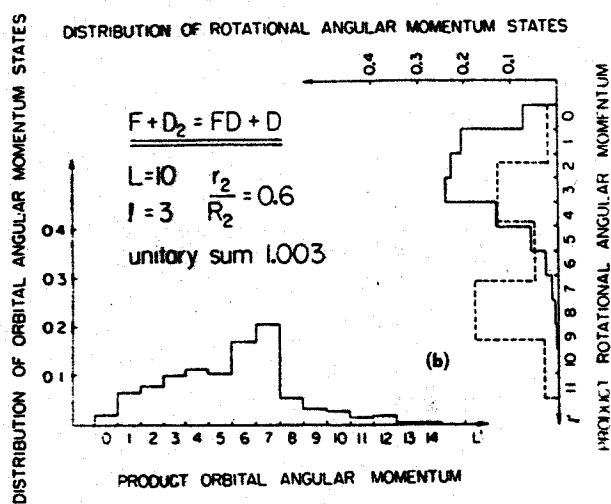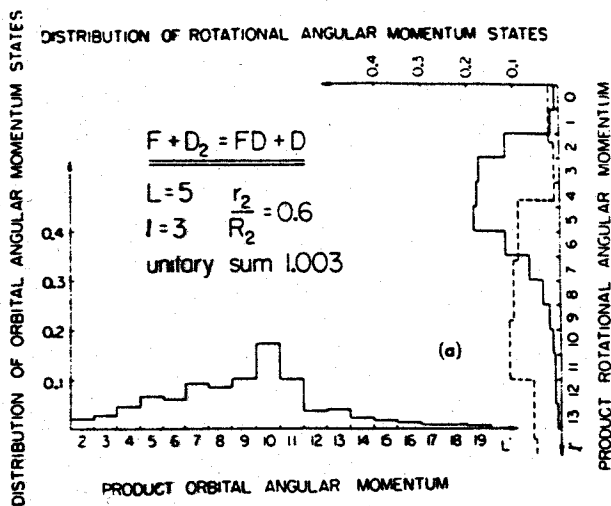
FIG. 13. Distribution of product orbital and rotational angular momenta for $F + D_2 = FD + D$ ($L = 5$, $l = 3$, $r_2/R_2 = 0.6$[18b]; trajectory results of Blais and Truhlar[18a] (——). (b) Distribution of product orbital and rotational angular momenta for $F + D_2 = FD + D$ ($L = 10$, $l = 3$, $r_2/R_2 = 0.6$)[18b]; trajectory results of Blais and Truhlar[18a] (——). (c) Distribution of product orbital and rotational angular momenta for $F + D_2 = FD + D$ ($L = 10$, $l = 3$, $r_2/R_2 = 0.8$)[18b]; trajectory results of Blais and Truhlar[18a] (——).

VI. REACTANT–PRODUCT TRANSFORMATION FOR RADIAL AND VIBRATIONAL WAVEFUNCTIONS

In the previous two sections, expansions have been derived which allow one to express the rotational part of the reactant scattering wavefunction in terms of product rotational states. The translational–vibrational part of the reactant wavefunctions also contributes to the product rotation. This is expressed in the case of planar reactive collisions by the expansion

$$F_{M-m}(N_1)v_{nm}(n_1) = \sum_t \mathcal{F}_{M-m,m,n,t}(N_2,n_2)y_0(t,\hat{N}_2,\hat{n}_2) , \quad (88)$$

where the functions $\mathcal{F}_{M-m,m,n,t}(N_2,n_2)$ are Fourier-cosine transforms of the radial functions

$$\mathcal{F}_{M-m,m,n,t}(N_2,n_2) = 2\int_0^{\tau} F_{M-m}(N_1)v_{nm}(n_1)\cos t\phi_2\,d\phi_2 . \quad (89)$$

For the definition of the coordinates, see Fig. 1. In the case that the transformation based on the solid harmonics is employed, the expansion (88) reads

$$\frac{F_{M-m}(N_1)}{N_1^{|M-m|}}\frac{v_{nm}(n_1)}{n_1^{|m|}} = \sum_t \mathcal{G}_{M-m,m,n,t}(N_2,n_2)y_0(t,\hat{N}_2,\hat{n}_2) , \quad (88')$$

where

$$\mathcal{G}_{M-m,m,n,t}(N_2,n_2) = 2\int_0^{\tau} \frac{F_{M-m}(N_1)}{N_1^{|M-m|}}\frac{v_{nm}(n_1)}{n_1^{|m|}}\cos t\,\phi_2\,d\phi_2 . \quad (89')$$

The evaluation of the integrals in Eqs. (89) and (89′) is the crucial step in evaluating the reactant–product transformation for a particular scattering case. Equations (89) or (89′) have to be evaluated for the whole series $t = 0,1,2,\cdots$ at every (N_2,n_2) necessary for the calculation scheme.

Because the reactant–product coordinate transformation conserves the length of the 4-vector (N_1,n_1), i.e., $N_1^2 + n_1^2 = N_2^2 + n_2^2$, the integration in Eqs. (89) and (89′) is along a circle around the origin in the N_1,n_1 plane with the radius $(N_2^2+n_2^2)^{1/2}$. The end points of the integration path are

$$(|N_2\cos\beta \mp n_2\sin\beta|, |N_2\sin\beta \pm n_2\cos\beta|) .$$

An integration path for a possible choice of (N_2,n_2) is presented in Fig. 14. A rough estimate as to around which t the series $\mathcal{F}_{M-m,m,n,t}(N_2,n_2)$ $[\mathcal{G}_{M-m,m,n,t}(N_2,n_2)]$ will have the dominant contributions can be made as follows: Let n_t be the number of oscillations of the translational wavefunction $F_{M-m}(N_2)$ along the integration path t and let n_v be the number of oscillations of the vibrational wavefunction $v_{nm}(n_1)$ along the integration path. The main contribution of the series then arises around $t = 2(n_t + n_v)$. Since the number of oscillations n_t and n_v increase with the local translational and vibrational momenta, respectively, a rise of the reactant translational or vibrational energy will shift the series $\mathcal{F}_{M-m,m,n,t}(N_2,n_2)$ or $\mathcal{G}_{M-m,m,n,t}(N_2,n_2)$ to higher t values.

The direction of the integration path in the N_1,n_1 plane (see Fig. 14) determines which degree of freedom, the translational degree of freedom or the vibrational degree of freedom, will contribute more to the product rotational state. For example, if the integration path is tilted towards the N_1 direction, the reactant transla-
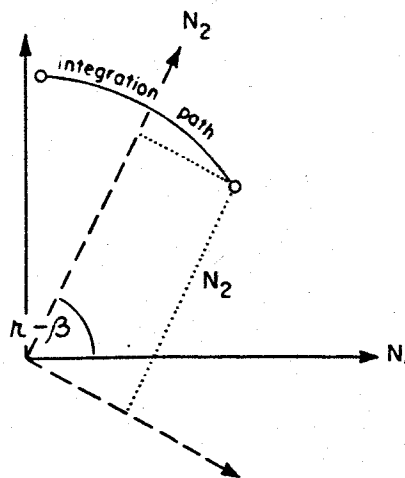

FIG. 14. Integral transformation of the radial and vibrational wavefunction—integration path in the N_1, n_1 plane.

tional motion will couple more strongly with the product internal rotation. If the integration path is more tilted towards the n_1 direction, the reactant vibrational motion will couple more strongly with the product internal rotation. The direction of the integration path, however, depends solely on the angle β and, therefore, solely on the masses of the colliding particles.

Let us illustrate the present discussion by considering as an example a reaction process $(1) + (2,3) \to (1,3) + (2)$, in which the transferred particle (3) is light compared with particles (1) and (2). In this case β is found to be small, so that the integration path in Fig. 14 would be tilted strongly towards the direction of the vibrational coordinate n_1. Hence, we can expect in the case of this reaction that the reactant vibration couples strongly with product rotations, whereas the coupling of reactant translation and product rotation should be weak. Furthermore, the discussion in Sec. V shows that in this case the orbital angular momentum of the reactants will preferentially go to the product orbital angular momentum, contributing only little to the product rotational angular momentum.

Since the evaluation of the integrals (89) and (89′) is the critical step of the transformation procedure, the choice between either the transformation (88), (89) or (88′), (89′) should be made on examination of the integrals in (89) and (89′). In case of large angular momentum values, the series of functions $\mathcal{G}_{M-m,m,n,t}(N_2,n_2)$ will be more slowly convergent than the series $\mathcal{F}_{M-m,m,n,t}(N_2,n_2)$. An *exception* is the case for which the rotational barrier is dominant over the potential terms in the collision complex region so that $F_{M-m}(N_2)$ $\sim N_2^{|M-m|}$ and $v_{nm}(n_2) \sim n_2^{|m|}$. However, because of the long range character of molecular potentials, this case will hardly occur. Hence, the range of angular momentum values will be the criterion for a choice between the two transformations. In the case that the orbital angular momentum values are large and the molecular rotational angular momentum values are small, it would be most appropriate to combine the two transformations.

Finally, for the case of three-dimensional reaction processes, we will give the integrals which allow us to evaluate the functions $\mathcal{F}_{L,l,n,t}(N_2, n_2)$ and $\mathcal{G}_{L,l,n,t}(N_2, n_2)$ defined in Eqs. (16) and (16'):

$$\mathcal{F}^{(1)}_{Lln,t}(N_2, n_2)$$

$$= (-1)^t \frac{\sqrt{2t+1}}{4\pi} \int_{-1}^{+1} d\cos\phi_2\, F_{Lln}(N_1) v_{nl}(n_1) P_t(\cos\phi_2) , \tag{90}$$

$$\mathcal{G}^{(1)}_{Lln,t}(N_2, n_2) = (-1)^t \frac{\sqrt{2t+1}}{4\pi}$$

$$\times \int_{-1}^{+1} d\cos\phi_2\, \frac{F_{Lln}(N_1)}{N_1^L} \frac{v_{nl}(n_1)}{n_1^l} P_t(\cos\phi_2) . \tag{90'}$$

The discussion about the integrals for the two-dimensional case holds for the integrals in Eqs. (90) and (90'), too, since (89), (89') and (90), (90') are related through[19]

$$P_t(\cos\phi) = \sum_{s=0}^{t} \frac{1}{4^t} \binom{2s}{s} \binom{2t-2s}{t-s} \cos(t-2s)\phi .$$

VII. SUMMARY

A transformation for three-particle reactive scattering wavefunctions in the coordinate representation which connects reactant and product states has been derived. For the purpose of the transformation, the wavefunction has been separated in a translational–vibrational and a rotational part. It has been shown how this transformation is contained implicitly in most approaches taken to solve the three-particle scattering problem. Further, it has been pointed out that this transformation can give rise to propensity rules for reactive transitions concerning the rotational states. The matrix elements of the reactant–product transformation in the total angular momentum basis are given in an analytical form. The accompanying transformation for the translational–vibrational wavefunction is of integral type, reflecting the nonlocal character of this transformation. Evaluation of the transformation matrix elements for the angular momentum state functions reveal that closed rotational channels have to be taken into account in order to make the reactant–product transformation complete. Algorithms have been derived to evaluate the angular matrix elements, even for very large quantum numbers which occur in many molecular reactions.   ◆

APPENDIX A: EVALUATION OF HYPERGEOMETRIC FUNCTIONS

Here we evaluate the functions $F_n^m(x)$ and $F^l_{1-l+n,l+n}(x)$, which are defined in Eqs. (33) and (65), respectively.

Let us first consider the evaluation of the series $F_n^m(x)$, $n = 0, \pm 1, \pm 2, \cdots$ ($m > 0, |x| < 1$). According to Eq. (33), two vectors of *contiguous* hypergeometric functions are needed:

$$_2F_1\left(\frac{m}{2}, n-\frac{m}{2}; n+1; x^2\right) \qquad n = 0, 1, 2, \ldots, N_1 , \tag{A1}$$

$$_2F_1\left(-\frac{m}{2}, n+\frac{m}{2}; n+1; x^2\right) \qquad n = 0, 1, 2, \ldots, N_2 . \tag{A2}$$

For m even, series (A1) is finite ($N_1 = \frac{1}{2}m$), since $F_n^m(x) = 0$ for $k \geq \frac{1}{2}m$. For m odd, $F_n^m(x)$ decays quickly to zero for $k > \frac{1}{2}m$, so that series (1) in this case can be terminated shortly beyond $k = (m+1)/2$. Series (A2), however, has to be generated over a wide range, especially if x lies in a small neighborhood near 1.

The scheme presented now for the evaluation of the series of hypergeometric functions (A1) and (A2) goes in three steps and is based on the contiguity relationship

$$_2F_1(a, -a+n-1; n; x^2) = \left[1 + \frac{n-2a}{n} x^2\right] {}_2F_1(a, -a+n; n+1; x^2)$$

$$- \frac{(n-a)(n-a+1)}{n(n+1)} x^2\, {}_2F_1(a, -a+n+1; n+2; x^2) , \tag{A3}$$

which is stable only in the direction of decreasing n.

Step 1: Evaluate $Z = F(a, -a+N, N+1; x^2)/F(a, -a+N-1, N; x^2)$ given by the Gauss continued fraction formula[20]

$$Z = \cfrac{1}{1 + \cfrac{a_1}{1 + \cfrac{a_2}{1 + \cdots}}} \tag{A4}$$

where

$$a_{2s-1} = (a+s-1)(a+s)x^2/(N+2s-3)(N+2s-2)$$

$$a_{2s} = (N+s-a-1)(N+s-a)x^2/(N+2s-2)(N+2s-1) .$$

The continued fraction (A4) is calculated best as $Z = \lim_{n \to \infty} (P_n/Q_n)$, where the P_n and Q_n are defined recursively by[21]

$$P_n = a_n P_{n-2} + P_{n-1}; \quad P_0 = 1; \quad P_1 = 1 ,$$

$$Q_n = a_n Q_{n-2} + Q_{n-1}; \quad Q_0 = 1; \quad Q_1 = 1 + a_1 . \tag{A5}$$

Step 2: Set $f_{N+1} = Z$ and $f_N = 1$ and generate the vector f_n, $n = N-1, N-2, \ldots, 0$ employing the recursion relationship (A3). The f_n all differ from the hypergeometric functions $F(a, -a+n; n+1; x^2)$ by a constant factor c_1. Similarly, the series $\hat{f}_n = c_2\, {}_2F_1(-a, a+n, n+1; x^2)$ can be evaluated. However, for $n = 0$,

$$f_0/c_1 = \hat{f}_0/c_2 ;$$

hence, setting $f_0 = \hat{f}_0$ implements $c_1 = c_2$.

Step 3: The unitary property of the $F_n^m(x)$ expressed by Eq. (40) reads

$$\sum_{n=0}^{N} \left(x^n \frac{\Gamma(1+m/2)}{\Gamma(n+1)\Gamma(1-n+m/2)} f_n \right)^2$$

$$+ \sum_{n=1}^{N} \left((-x)^n \frac{\Gamma(n+m/2)}{\Gamma(n+1)\Gamma(m/2)} \hat{f}_n \right)^2 = c_1^2 . \tag{A6}$$

Thus, the unknown factor c_1 is determined and, finally,

$$F_n^m(x) = x^n \frac{\Gamma(1+m/2)}{\Gamma(n+1)\Gamma(1-n+m/2)} f_n/c_1 \qquad n \geq 0$$

$$F_n^m(x) = (-x)^n \frac{\Gamma(-n+m/2)}{\Gamma(-n+1)\Gamma(m/2)} \hat{f}_{-n}/c_1 \qquad n \leq 0 . \tag{A7}$$

Note that in the numerical scheme presented, the explicit evaluation of the hypergeometric functions that define the coefficients $F_n^m(x)$ is not necessary! How-

ever, to determine the normalization constant c_1 properly, it is important to choose N large enough to assure convergence of the sum in Eq. (A6).

In the three-dimensional case, the transformation coefficients for reactant orbital and rotational angular momenta $F_{l-i+n, i+n}^{l}(x)$, $i = 0, 1, 2, \cdots l$; $n = 0, 1, 2, \ldots$, are proportional to

$$\mathfrak{F}_{in} = {}_2F_1\left(i - \frac{l+1}{2}, \frac{l}{2}+n; i+n+\frac{3}{2}; x^2\right) . \tag{A8}$$

The $\mathfrak{F}_{in}$ form a $(l+1) \times \infty$-matrix $\mathfrak{F}$ of *contiguous* hypergeometric functions. Because of their unitarity, the $F_{l', l''}^{l}(x)$ must converge to zero over a finite range;

hence, one needs to construct $\mathfrak{F}$ only over a finite $N \times N$ range, for some properly chosen N. From Eq. (65) one can conclude that the convergence of $F_{l-i+n, i+n}^{l}(x)$ is governed mainly by the factor x^{i+n}, so that the coefficients can be expected to converge equally fast in the i- and the n direction. As in the two-dimensional case, $\mathfrak{F}$ has to be known only within a constant factor c, which can later be obtained from Eq. (71'), which states that the $F_{l-i+n, i+n}^{l}(x)$ should be normalized to one. For that reason, the hypergeometric functions that make up the matrix $\mathfrak{F}$ need not be calculated explicitly; only their relative ratios need to be determined. The numerical procedure to obtain the $F_{l-i+n, i+n}^{l}(x)$ is then as follows:

(1) Evaluate the ratio $Z = \mathfrak{F}_{NN}/\mathfrak{F}_{N, N-1}$ by applying the Gauss continued fraction formula (A4). Set $\mathfrak{F}_{NN} = Z$ and $\mathfrak{F}_{N, N-1} = 1$.

(2) Evaluate the row $\mathfrak{F}_{Ni}$, $i = 0, 1, 2, \ldots, N-2$ through recursive application of the contiguity relationship

$$_2F_1(a, b-1; c-1; x^2) = \frac{c-1+(b-a)x^2}{(c-1)} \, _2F_1(a, b; c; x^2) - \frac{b(c-a)x^2}{c(c-1)} \, _2F_1(a, b+1; c+1; x^2) , \tag{A9}$$

which relates $\mathfrak{F}_{N, i+1}$, $\mathfrak{F}_{Ni}$, and $\mathfrak{F}_{N, i-1}$. To evaluate the neighboring row $\mathfrak{F}_{N-1, i}$, $i = N, N-1, \ldots, 0$, use the contiguity properties

$$_2F_1(a-1, b; c-1; x^2) = \frac{(a-b)}{(c-1)} x^2 \, _2F_1(a, b; c; x^2) + \, _2F_1(a, b-1; c-1; x^2) , \tag{A10}$$

which relates $\mathfrak{F}_{NN}$, $\mathfrak{F}_{N, N-1}$, and $\mathfrak{F}_{N-1, N}$, and

$$_2F_1(a-1, b; c-1; x^2) = -\frac{b(c-a)}{c(c-1)} x^2 \, _2F_1(a, b; c; x^2) + \, _2F_1(a, b+1; c+1; x^2) , \tag{A11}$$

which relates $\mathfrak{F}_{Ni}$, $\mathfrak{F}_{N, i+1}$, and $\mathfrak{F}_{N-1, i}$. Generate from the Nth and the $(N-1)$th rows all remaining elements by recursion down the columns applying formula (A9) with a and b interchanged. The elements $\mathfrak{F}_{in}$ of $\mathfrak{F}$ have to be multiplied by the factor

$$(-x)^{i+n} \frac{\sqrt{\pi}}{2}[(2l-2i+2n+1)(2i+2n+1)]^{1/2} \frac{\Gamma[(l+3)/2]}{\Gamma(l/2)} \frac{\Gamma(n+l/2)}{\Gamma(i+n+3/2)\Gamma[(l+3)/2-i]} \begin{pmatrix} l & l-i+n & i+n \\ 0 & 0 & 0 \end{pmatrix} \tag{A12}$$

in order to obtain $F_{l-i+n, i+n}^{l}(x)$.

Rewriting the parity coefficient

$$\begin{pmatrix} l & l-i+n & i+n \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{\sqrt{\pi}} \frac{(-1)^{i+n}}{(2l+2n+1)^{1/2}} \left[\frac{\Gamma(l+n+1)}{\Gamma(l+n+1/2)} \frac{\Gamma(n+1/2)}{\Gamma(n+1)} \frac{\Gamma(i+1/2)}{\Gamma(i+1)} \frac{\Gamma(l-i+1/2)}{\Gamma(l-i+1)}\right]^{1/2} , \tag{A13}$$

(A12) can be expressed in the form (A14), which is more suitable for numerical evaluation.

(3) Perform the multiplication on the $\mathfrak{F}_{in}$ according to

$$F_{l-i+n, i+n}^{l}(x) = (-1)^l \left[\prod_{r=1}^{l} \frac{r}{r-1/2}\right]^{1/2} \cdot \prod_{s=1}^{i} \left\{x \frac{l/2+3/2-s}{s+1/2}\left[\frac{s-1/2}{s} \frac{l-s}{l-s-1/2}\right]^{1/2}\right\}$$

$$\times \left(\frac{(2l-2i+2n+1)(2i+2n+1)}{(2l+2n+1)}\right)^{1/2} \prod_{t=1}^{n} \left\{(-x)\frac{t+l/2-1}{i+t+1/2}\left[\frac{t-1/2}{t} \frac{l+t}{l+t-1/2}\right]^{1/2}\right\} \mathfrak{F}_{in} . \tag{A14}$$

Because of the unknown factor c contained in $\mathfrak{F}_{in}$, the transformation coefficients $F_{l-i+n, i+n}^{l}(x)$ in general will not be normalized, but

$$\sum_{i, n} [F_{l-i+n, i+n}^{l}(x)]^2 = c^2 . \tag{A15}$$

Hence, it remains to divide the transformation coefficients by the constant c thus obtained. The proper sign of c is obtained through the collinear sum rule, Eq. (70).

APPENDIX B: PROOF OF ORTHOGONALITY RELATIONS

The orthogonality relationship for $F_{l', l''}^{l}(x)$ is as follows:

Multiplying (67) by its conjugate complex and summing over m gives

$$\frac{1}{4\pi} = \sum_{l',l'',L',L'',m} [(2l'+1)(2L'+1)]^{1/2}(-1)^{l'+l''+L'+L''}\begin{pmatrix} l' & l'' & l \\ 0 & m & -m \end{pmatrix}$$

$$\times \begin{pmatrix} L' & L'' & l \\ 0 & m & -m \end{pmatrix} F^l_{l'\cdot l''}(x) F^l_{L'\cdot L''}(x) Y_{l''\cdot m}(\hat{c}-\hat{b},0) Y^*_{L''\cdot m}(\hat{c}-\hat{b},0) . \tag{B1}$$

Coupling together the spherical harmonics by virtue of

$$Y_{l''\cdot m}(\hat{c}-\hat{b},0) Y^*_{L''\cdot m}(\hat{c}-\hat{b},0) = (-1)^m \sum_{\lambda} \left[\frac{(2l''+1)(2L''+1)(2\lambda+1)}{4\pi}\right]^{1/2} \begin{pmatrix} l'' & L'' & \lambda \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} l'' & L'' & \lambda \\ 0 & 0 & 0 \end{pmatrix} Y_{\lambda 0}(\hat{c}-\hat{b},0) , \tag{B2}$$

and carrying out the sum over m using[22]

$$\sum_m (-1)^m \begin{pmatrix} l' & l'' & l \\ 0 & m & -m \end{pmatrix} \begin{pmatrix} L' & L'' & l \\ 0 & m & -m \end{pmatrix} \begin{pmatrix} l'' & L'' & \lambda \\ m & -m & 0 \end{pmatrix} = \begin{pmatrix} L' & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L' & l' & \lambda \\ l'' & L'' & l \end{Bmatrix} , \tag{B3}$$

one gets

$$\frac{1}{\sqrt{4\pi}} = \sum_{\lambda} \sum_{l',l'',L',L''} \begin{pmatrix} l'' & L'' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L' & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L' & l' & \lambda \\ l'' & L'' & l \end{Bmatrix}$$

$$\times [(2l'+1)(2l''+1)]^{1/2} F^l_{l'\cdot l''}(x)[(2L'+1)(2L''+1)]^{1/2} F^l_{L'\cdot L''}(x) Y_{\lambda 0}(\hat{c}-\hat{b},0) . \tag{B4}$$

From this, (71) follows immediately.

Orthogonality relationships for ${}_3C^J_{Ll,L'\cdot l'}(N_1,n_1)$: To derive the orthogonality relationships for the ${}_3C^J_{Ll,L'\cdot l'}(N_2,n_2)$, we start from

$$\sum_{J,M} \mathcal{Y}_{JM}(L,l;\hat{N}_1,\hat{n}_1)\mathcal{Y}^*_{JM}(L,l;N_1,n_1) = (2L+1)(2l+1)/(4\pi)^2 . \tag{B5}$$

Application of Eq. (74) to replace the reactant angular momentum wavefunctions by product angular momentum wavefunctions gives, after performing some coupling algebra,

$$\frac{(2L+1)(2l+1)}{4\pi} = \sum_{\lambda} \sum_{J} \sum_{\substack{L',l'; \\ L'',l''}} (-1)^J(2J+1) \, {}_3C^J_{Ll,L'\cdot l'} \, {}_3C^J_{Ll,L''\cdot l''}$$

$$\times [(2\lambda+1)(2L'+1)(2L''+1)(2l'+1)(2l''+1)]^{1/2} \begin{pmatrix} L' & L'' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l'' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l'' & l' & \lambda \\ L' & L'' & J \end{Bmatrix} \mathcal{Y}_{00}(\lambda,\lambda;\hat{N}_2,\hat{n}_2) . \tag{B6}$$

Observing that the left side of this equation is constant while the right side exhibits an angular dependence, we are led to Eqs. (78).

APPENDIX C: EVALUATION OF 9j COEFFICIENTS[23]

The convolution of $F^L_{L_1L_2}(x_1)$ and $F^l_{l_1l_2}(x_2)$ according to Eq. (75) to yield the coefficients ${}_3C^J_{Ll,L'\cdot l'}(N_2,n_2)$ can volve very large angular momentum quantum numbers. Formulas (A14) for the series of $F^L_{L_1L_2}(F^l_{l_1l_2})$ coefficients and (A13) for the parity coefficients are stable for large quantum numbers, so that no special consideration needs to be given to the evaluation of these quantities. However, to our knowledge no general method exists for the evaluation of 9j coefficients containing large quantum numbers. We suggest the following algorithm to obtain 9j coefficients quickly and accurately for all ranges of quantum numbers. We start from the expansion:

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & j_9 \end{Bmatrix} = \sum_{\kappa} (-)^{2\kappa}(2\kappa+1) \begin{Bmatrix} \kappa & j_9 & j_1 \\ j_7 & j_4 & j_8 \end{Bmatrix} \begin{Bmatrix} \kappa & j_9 & j_2 \\ j_5 & j_9 & j_4 \end{Bmatrix} \begin{Bmatrix} \kappa & j_1 & j_9 \\ j_3 & j_9 & j_2 \end{Bmatrix} .$$

To evaluate the 9j coefficient, three strings of 6j coefficients

$$\begin{Bmatrix} \kappa & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{Bmatrix} , \quad \max\{|l_2-l_3|, |l_5-l_6|\} \le \kappa \le \min\{l_2+l_3, l_5+l_6\} ,$$

are needed. The elements in these strings can be generated by use of the recursion relationship[24]

$$\begin{Bmatrix} \kappa & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{Bmatrix} = [(\kappa-1)^2(\kappa+l_2+l_3+1)(\kappa-l_2+l_3)(\kappa+l_2-l_3)(-\kappa+l_2+l_3+1)(\kappa+l_5+l_6+1)(\kappa-l_5+l_6)(\kappa+l_5-l_6)(-\kappa+l_5+l_6+1)]^{-1/2}$$

$$\times \Bigg[-(2\kappa-1)2[l_2(l_2+1)l_5(l_5+1)+l_3(l_3+1)l_6(l_6+1)-\kappa(\kappa-1)l_4(l_4+1)] - [l_2(l_2+1)+l_3(l_3+1)-\kappa(\kappa-1)]$$

$$\times [l_5(l_5+1)+l_6(l_6+1)-\kappa(\kappa-1)]\begin{Bmatrix} \kappa-1 & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{Bmatrix} - [\kappa^2(\kappa+l_2+l_3)(\kappa-l_2+l_3-1)(\kappa+l_2-l_3-1)$$

$$\times (-\kappa+l_2+l_3+2)(\kappa+l_5+l_6)(\kappa-l_5+l_6-1)(\kappa+l_5-l_6-1)(-\kappa+l_5+l_6+2)]^{1/2}\begin{Bmatrix} \kappa-2 & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{Bmatrix} \Bigg] \tag{C1}$$

once proper starting values are given. The start of the recursion can be simplified by observing that if κ is set to $l_{min}+1$ ($l_{max}+1$), the recursion involves only the first (last) two $6j$ coefficients. Since the recursion formula is linear, one may arbitrarily set

$$\begin{Bmatrix} l_{min} & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{Bmatrix} = 1 \, ,$$

so that all $6j$ coefficients generated are off by a common factor. This factor can be determined from the unitary property

$$\sum_{\kappa} (2\kappa+1)(2l_4+1) \begin{Bmatrix} \kappa & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{Bmatrix}^2 = 1 \qquad (C2)$$

together with the phase convention

$$\mathrm{sgn}\left(\begin{Bmatrix} l_{max} & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{Bmatrix}\right) = (-)^{l_2+l_3+l_5+l_6} \, . \qquad (C3)$$

To assure numerical stability, the recursion should be performed from both ends of the κ range. Hence, one starts from

$$\begin{Bmatrix} l_{min} & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{Bmatrix} = 1$$

and from

$$\begin{Bmatrix} l_{max} & l_2 & l_3 \\ l_4 & l_5 & l_6 \end{Bmatrix} = 1$$

towards a middle κ value, matches the recursion series thereby rescaling one of the series, and finally normalizes the $6j$ coefficients by use of Eqs. (C2) and (C3).

APPENDIX D: EVALUATION OF $_2C_{mm'}^M$ AND $_3C_{LI,L'I'}^J$ FOR THE TWO LIMITING CASES OF HEAVY ATOM AND LIGHT ATOM TRANSFER REACTIONS

In the case of heavy atom transfer reactions, i.e., $m_3 \to \infty$, the arguments (51a) and (51b) entering into the evaluation of the coupling coefficients are $(N_2/n_2)\tan\beta = -\infty$ and $(n_2/N_2)\tan\beta = -\infty$. For the two-dimensional case we have from Eq. (39) together with Eq. (33)

$$\lim_{x\to\infty} F_k^m(\alpha x) = (\mathrm{sgn}\alpha)^m \delta_{km} \, ,$$

hence

$$_2C_{mm'}^M = (-1)^{M-m} \sum_k \delta_{k+m'-m,M-m}\delta_{km} = (-1)^{M-m}\delta_{m',M-m} \, .$$

For the three-dimensional case we have, from Eqs. (69) and (65),

$$\lim_{x\to\infty} F_{i'i''}^l(\alpha x) = (\mathrm{sgn}\alpha)^l \delta_{i'0}\delta_{i''l} \, ;$$

hence,

$$_3C_{LI,L'I'}^J = (-1)^l[(2L+1)(2l+1)(2L'+1)(2l'+1)]^{1/2}$$

$$\times \begin{Bmatrix} L & l & J \\ 0 & l & L' \\ L & 0 & l' \end{Bmatrix} \begin{pmatrix} 0 & l & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & 0 & l' \\ 0 & 0 & 0 \end{pmatrix} \, .$$

From

$$\begin{pmatrix} 0 & l & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & 0 & l' \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{L+l}[(2l+1)(2L+1)]^{-1/2}\delta_{lL'}\cdot\delta_{Ll'}$$

and

$$\begin{Bmatrix} L & l & J \\ 0 & l & L' \\ L & 0 & l' \end{Bmatrix} = [(2l+1)(2L+1)]^{-1}(-1)^{J+L+l} \, ,$$

we get $_3C_{LI,L'I'}^J = (-1)^{J+l}\delta_{lL}\cdot\delta_{Ll'}$.

In the case of light atom transfer reactions, i.e., $m_3 = 0$, the arguments (51a) and (51b) are $(n_2/N_2)\tan\beta = 0$ and $(N_2/n_2)\tan\beta = -R_2/r_2$. We have then, for two-dimensional reactions from $F_k^m(0) = \delta_{k0}$,

$$_2C_{mm'}^M(N_2,n_2) = (-1)^M F_{m-m}^M\left(-\frac{R_2}{r_2}\right),$$

and for three-dimensional reactions from $F_{L_1L_2}^L = \delta_{LL_1}\delta_{L_20}$,

$$_3C_{LI,L'I'}^J(N_2,n_2)$$
$$= (-1)^{J+L}\sum_{l_1}[(2L+1)(2l+1)(2l_1+1)(2L'+1)]^{1/2}$$

$$\times \begin{Bmatrix} L' & l_1 & L \\ l & J & l' \end{Bmatrix} \begin{pmatrix} L & l_1 & L' \\ 0 & 0 & 0 \end{pmatrix} F_{l'l_1}^l\left(-\frac{R_2}{r_2}\right).$$

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