Quantum Mechanical Propensity Rules
for the Transfer of Angular Momentum in Three-Atom Reactions

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In the following note I want to give a brief account of the quantum-mechanical transformation which connects the reactant and product angular momentum states in three-atom reactions [1]. This transformation is a necessary step in most formulations of the quantum-mechanical reactive scattering problem. As molecular reactions often involve a great number of open rotational channels, and also large angular momentum quantum numbers, actual calculations require a transformation method which is both numerically convenient and stable in the limit of large quantum numbers.

For the well-known nj-coupling coefficients, which describe the decomposition and addition of angular momentum states defined in the same coordinate system, such algorithm has been developed recently [2, 3].

For molecular reactions $A + BC \rightarrow AB + C$, however, reactant and product states are defined in terms of different coordinates R_1, r_1 and R_2, r_2, respectively, which are presented in Fig. 1. In this case the decomposition of reactant angular momenta in terms of product angular momenta cannot be described by Wigner's nj-coefficients which depend only on
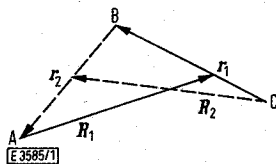
Fig. 1

Reactant and product coordinates for the reaction $A + BC \rightarrow AB + C$. R_1 goes from atom A to the center of mass of BC, R_2 goes from atom C to the center mass of AB

the angular momentum quantum numbers. Instead, it is described by new coupling coefficients $C^J_{Ll,L'l'}$ which in fact depend on the masses of the reacting particles m_A, m_B, m_C and on the geometry of the reaction complex. The coefficients $C^J_{Ll,L'l'}$ have been derived in Ref. [1]. With the reactant total angular momentum state

$$Y_{JM}(Ll;\hat{R}_1,\hat{r}_1) = \sum_{m_L,m_l} (Lm_L, lm_l | JM) Y_{Lm_L}(\hat{R}_1) Y_{lm_l}(\hat{r}_1) \quad (1a)$$

and the product total angular momentum state

$$Y_{JM}(L'l';\hat{R}_2,\hat{r}_2) = \sum_{m'_L,m'_l} (L'm'_L, lm'_l | JM) Y_{L'm'_L}(\hat{R}_2) Y_{l'm'_l}(\hat{r}_2) \quad (1b)$$

where L (L') denotes the orbital and l (l') the rotational angular momentum quantum number, the reactant-product coupling coefficients $C^J_{Ll,L'l'}$ are defined through the expansion

$$Y_{JM}(L,l;\hat{R}_1,\hat{r}_1) = \sum_{L',l'} C^J_{Ll,L'l'} Y_{JM}(L',l';\hat{R}_2,\hat{r}_2). \quad (2)$$

The coupling coefficients $C^J_{Ll,L'l'}$ bear an important physical meaning. They give rise to propensity rules for the transfer of angular momentum from reactants to products in reactive collisions, resembling in this respect the Franck-Condon coefficients of vibrational transitions. This will be demonstrated below for the case of the reaction $K + HBr \rightarrow KBr + H$.

The basic task for the reactant-product angular momentum transformation is to express a rotation around a vector a in terms of rotations around the vectors b and c when $a = \beta b + \gamma c$. This is done by the addition theorem [1]

$$Y_{lm}(\hat{a}) = \sqrt{4\pi}(\text{sgn}\,\beta)^l \sum_{l',l''} F^l_{l'l''}(\gamma c/\beta b) \, Y_{lm}(l',l'';\hat{b},\hat{c}) \quad (3)$$

for Y_{lm} as defined in (1a, b). The coupling coefficients $F^l_{l'l''}$ are given by the analytical expression ($|x| < 1$):

$$F^l_{l'l''}(x) = \frac{\sqrt{\pi}}{2} [(2l'+1)(2l''+1)]^{1/2}(-1)^{(l+l'+l'')/2}$$

$$\cdot \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} \frac{\Gamma[(l+3)/2]}{\Gamma(l/2)} \frac{\Gamma[(l'+l'')/2]}{\Gamma(l''+\frac{3}{2})\Gamma[(l'-l''+3)/2]} x^{l''} \quad (4)$$

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

They obey the symmetry relationships

$$F^l_{l'l''}(x) = (-1)^{l''} F^l_{l'l''}(-x) \quad (6a)$$

$$F^l_{l'l''}(x) = (\text{sgn}\,x)^l F^l_{l''l'}(x^{-1}) \quad (6b)$$

and the sum rules

$$\sum_{\substack{l',l'' \\ L',L''}} \begin{pmatrix} l' & L & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'' & L'' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & l' & \lambda \\ l'' & L'' & l \end{Bmatrix} [(2l'+1)(2l''+1)]^{1/2} F^l_{l'l''}(x)$$

$$\cdot [(2L'+1)(2L''+1)]^{1/2} F^l_{L'L''}(x) = \delta_{\lambda 0} \quad (7a)$$

(for $\lambda = 0$ this reduces to $\sum_{l',l''} [F^l_{l'l''}(x)]^2 = 1$) and

$$\sum_{l',l''} [(2l'+1)(2l''+1)]^{1/2} F^l_{l'l''}(|x|)\begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix} = (-1)^l. \quad (7b)$$

For the evaluation of the $F^l_{l'l''}$ coefficients an efficient and stable $(L, l \rightarrow \infty)$ algorithm has been derived [1].
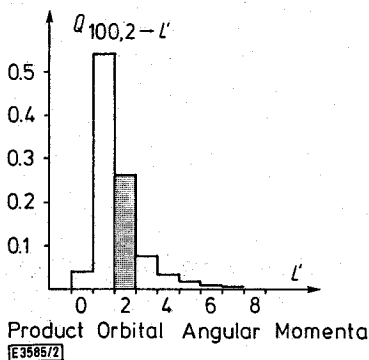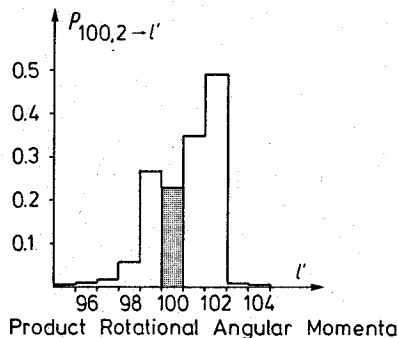

Fig. 2

Distribution of product rotational and orbital angular momenta for the reaction $K + HBr \rightarrow KBr + H$ ($L = 100, l = 2, r_2/R_2 = 2.5$) evaluated according to Equations (11a, b)

In order to simplify the decomposition of the reactant rotational states (1a) in terms of the product rotational states (1b) we introduce the Jacobi coordinates N_1, n_1 and N_2, n_2 through [4]

$$N_1 = \alpha_1^{-1} R_1; \quad n_1 = \alpha_1 r_1$$

$$\alpha_1^2 = [m_C m_B (m_A + m_B + m_C)/m_A(m_B + m_C)^2]^{1/2} \quad (8)$$

(similarly for N_2, n_2). The transformation connecting reactant and product coordinates is then

$$N_1 = \cos\beta \, N_2 - \sin\beta \, n_2$$

$$n_1 = \sin\beta \, N_2 + \cos\beta \, n_2 \quad (9)$$

where $\cos\beta = -[m_A m_C/(m_A + m_B)(m_B + m_C)]^{1/2}$ and $\sin\beta > 0$. We apply then the decomposition (3) to the reactant total angular momentum state (1a), viz. to the orbital angular momentum state $Y_{Lm_L}(\hat{N}_1)$ and to the rotational angular momentum state $Y_{lm_l}(\hat{n}_1)$, couple the resulting product states to total angular momentum states, and obtain the expansion (2) where [5]

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

$$\cdot (2L'+1)(2l+1)(2l_1+1)(2l_2+1)(2l'+1)]^{1/2}$$

$$\cdot \begin{Bmatrix} L & l & J \\ L_1 & l_1 & L' \\ L_2 & l_2 & l' \end{Bmatrix} \begin{pmatrix} L_1 & l_1 & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_2 & l_2 & l' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\cdot F^L_{L_1 L_2}\left(-\frac{n_2}{N_2}\tan\beta\right) F^l_{l_2 l_1}\left(\frac{N_2}{n_2}\tan\beta\right). \tag{10}$$

In closing we would like to demonstrate the propensity rules predicted by the $C^J_{Ll,L'l'}$ coefficients and present in Fig. 2 the distributions of the product rotational and orbital angular momentum states evaluated by virtue of

$$P_{L,l \to l'} = \sum_{J,L'} [(2J+1)/(2L+1)(2l+1)]|C^J_{Ll,L'l'}|^2 \tag{11a}$$

and

$$Q_{L,l \to L'} = \sum_{J,l'} [(2J+1)/(2L+1)(2l+1)]|C^J_{Ll,L'l'}|^2 \tag{11b}$$

respectively, for the reaction K + HBr → KBr + H with the initial orbital and rotational angular momentum quantum numbers $L = 100$ and $l = 2$. Fig. 2 demonstrates that in the course of this reaction in which the heaviest atom is transferred, orbital and rotational angular momenta are approximately exchanged, i.e. $L' \sim 2$, $l' \sim 100$. Beside confirming this well-known behaviour, Fig. 2 presents the complete distributions to be expected for the product angular momentum states in case that there is no coupling between the rotational and the translational, vibrational degress of freedom.

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[5] In Ref. [1] have been derived also transformation coefficients $D^J_{Ll,L'l'}$ based on solid spherical harmonics $[r^l Y_{lm}(\hat{r})]$ for the description of the angular momentum states.