Selection rules and quasi selection rules in three-body exchange reactions†

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The coupled γ operator formalism is applied to derive exact and approximate selection rules that govern the rotational state distribution of products following an interaction between a diatomic molecule and a free atom. The analysis is performed for a two-channel system in which one of the atoms is infinitely heavy.

1. INTRODUCTION

In the past few years extensive work has been done on the quantum mechanical three-body exchange interaction. Most of it was performed restricting the three particles to moving on a straight line—i.e. the collinear system†. Only very recently were efforts extended towards the coplanar system (where the motion of the three particles is constrained to a fixed plane) and the three-dimensional system [2].

Recently an integral equation formalism has been presented, which enables the study of exchange interactions between a bound system of two particles and a third free particle [3]. Also several examples were worked out by which the efficiency of the method was proved, both as an analytical tool to get a deeper insight into the nature of the interaction and as a device for obtaining numerical results [4].

In this work use will be made of this formalism to extract selection rules and quasi selection rules that govern the rotational state distribution of products resulting from a certain type of three-body interaction. The system that will be considered is composed of three atoms, A, B, and C, where the initial bound system is assumed to be BC, and A is the free particle. The final product might be either an excited molecule BC with A free again (inelastic collision) or a new grouping in which A and B are bound and C is free (exchange collision). The channels for creating either the bound system AC or the three free particles are assumed to be closed. In addition, atom B is infinitely heavy and the interaction is assumed to occur on a single potential energy surface.

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† Since the literature on the collinear system is very extensive, we will mention only the detailed study by Truhlar and Kuppermann [1] and a recent review of the field by Levine [1]. Each of these includes an extensive list of references.
2. THE COUPLED SYSTEM OF INTEGRAL EQUATIONS

The formalism is based on the concept of the channel operators, \( \tau_{\alpha\alpha} \) and \( \tau_{\beta\alpha} \), which are related to the transition probabilities for going from an initial channel configuration \( \alpha^0 \) in state \( |\theta(\nu_\alpha^0)\rangle \) to either a final channel configuration \( \alpha \) in state \( |\theta(\nu_\alpha)\rangle \) or to a final configuration channel \( \beta \) in state \( |\theta(\nu_\beta)\rangle \) (\( \nu_\rho \) stands for a grouping of quantum numbers that characterizes the \( \rho \)th state). It has been shown that these two operators satisfy the following coupled system of equations: \[ [3\ a] \]

\[
\begin{align*}
\tau_{\alpha\alpha} &= V_{\alpha} + V_{\alpha} G_{0\beta} \tau_{\beta\alpha}^+, \\
\tau_{\beta\alpha} &= V_{\alpha} + V_{\beta} G_{0\alpha} \tau_{\alpha\alpha}^+,
\end{align*}
\]

where \( V_\rho \) is the perturbation in the \( \rho \)th channel and \( G_{0\rho}^+ \) is the free Green's function in that channel:

\[ [2] \]

\[
G_{0\rho}^+ = (E - K_\rho + i\epsilon)^{-1}.
\]

\( E \) is the total energy and \( K_\rho \) is the unperturbed Hamiltonian.

Equations (1) were shown \[ [3\ b] \] to evolve into the following system of integral equations:

\[ [3] \]

\[
\begin{align*}
\frac{1}{R_\alpha} \chi_\alpha(\nu_\alpha|R_\alpha) &= \int_0^\infty d r_\alpha \int_{-1}^1 d(\cos \lambda_\alpha) u^*(\nu_\alpha|r_\alpha) V_\alpha(r_\alpha, R_\alpha, \lambda_\alpha) \\
&\times \langle \nu_\alpha | \Omega(\lambda_\alpha, \lambda_{\alpha\beta}, \lambda_\beta) | \nu_\beta \rangle \left( \frac{E - K_\beta + i\epsilon}{R_\beta} \right), \\
\frac{1}{R_\beta} \chi_\beta(\nu_\beta|R_\beta) &= \int_0^\infty d r_\beta \int_{-1}^1 d(\cos \lambda_\beta) u^*(\nu_\beta|r_\beta) V_\beta(r_\beta, R_\beta, \lambda_\beta) \\
&\times \langle \nu_\beta | \Omega(\lambda_\beta, \lambda_{\beta\alpha}, \lambda_\alpha) | \nu_\alpha \rangle \left( \frac{E - K_\alpha + i\epsilon}{R_\alpha} \right),
\end{align*}
\]

where \( \chi_\rho(\nu_\rho|R_\rho) \) are the functions to be obtained and which yield the \( \tau \)-matrix elements through the integral

\[ [4] \]

\[
\langle \nu_\alpha | \tau_{\rho\alpha} | \nu_\alpha \rangle = \int_0^\infty d R_\rho j(\nu_\rho|R_\rho) \chi_\rho(\nu_\rho|R_\rho).
\]

† Again, the literature is too extensive to list; we will mention only a few textbooks in which most of the references can be found \[ [5] \].
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Here \( j(v_\rho | R_\rho) \) is a Ricatti–Bessel function. The functions \( u(v_\rho | r_\rho) \) are the vibrational eigenfunctions of the molecule, the variables \( r_\rho \) and \( R_\rho \) stand for the internal coordinate and the relative motion coordinate, \( \lambda_\rho \) is the angle between \( r_\rho \) and \( R_\rho \), and \( \lambda_{\rho \rho'} \) is the angle between \( R_\rho \) and \( R_{\rho'} \).

The functions \( F_\rho(v_\rho | R_\rho) \) stand for

\[
F_\rho(v_\rho | R_\rho) = \frac{1}{K(v_\rho)} \int_0^\infty dR_\rho' \chi_\rho(v_\rho | R_\rho') j(v_\rho | R_\rho') h(v_\rho | R_\rho' >),
\]

where \( h(v_\rho | R_\rho) \) is spherical Hankel function multiplied by \( K(v_\rho) \). \( R_\rho \) and \( R_< \) and \( R_> \) represent the lesser and the greater of \( R \) and \( R' \).

The matrix elements \( \langle \nu_\rho' | \Omega | \nu_\rho > \) stand for

\[
\langle \nu_\rho' | \Omega(\lambda_\rho' , \lambda_{\rho \rho' } , \lambda_\rho ) | \nu_\rho > = \int d\omega \Lambda^*(\nu_\rho' | \epsilon_{\rho'} , \hat{R}_{\rho'} ) \Lambda(\nu_\rho' | \epsilon_{\rho} , \hat{R}_{\rho} ),
\]

where \( \Lambda(\nu_\rho' | \epsilon_{\rho'} , \hat{R}_{\rho'} ) \) is the angular dependence part of the full eigenvector of the unperturbed Hamiltonian \( K_\rho \), and \( \omega \) stands for the three Euler angles \( \phi, \Theta, \Phi \).

In case the atom that corresponds to the closed channel is infinitely heavy the following simplifications can be introduced :

\[
r_\rho = R_{\rho'}, \quad \lambda_\rho = \lambda_{\rho'}, \quad \rho \neq \rho'.
\]

Having introduced these relations the integration over the distances becomes independent of the integration over the angles, and consequently the latter can be performed directly. In what follows we will treat explicitly the first equation only. To do this let us write the potential in the form

\[
V_\rho(R_\beta, R_\alpha, \lambda) = \sum \nu_\rho V_\rho'(R_\beta, R_\alpha) P_\rho(\cos \lambda).
\]

Thus equation (8) can be rewritten

\[
\chi_\alpha(v_\alpha | R_\alpha) = j(v_\alpha^0 | R_\alpha) \sum \frac{1}{1} \int_{-1}^{1} d(\cos \lambda) P_\rho(\cos \lambda) \langle \nu_\alpha | \Omega(\lambda, 0, \lambda) | \nu_\alpha^0 >
\]

\[
\times \int_0^\infty dR_\beta u^*(v_\alpha | R_\beta) V_\rho'(R_\beta, R_\alpha) u(v_\alpha^0 | R_\beta)
\]

\[
- \sum_{\nu_\beta} u(v_\beta | R_\alpha) \sum \frac{1}{1} \int_{-1}^{1} d(\cos \lambda) P_\rho(\cos \lambda) \langle \nu_\alpha | \Omega(\lambda, \lambda, \lambda) | \nu_\beta >
\]

\[
\times \int_0^\infty dR_\beta u^*(v_\alpha | R_\beta) V_\rho'(R_\beta, R_\alpha) F_\rho(v_\beta | R_\beta).
\]

We will introduce the following notations :

\[
\langle \nu_\rho | A_\rho'(R_\rho') | \nu_\rho > = -i u(v_\rho' | R_\rho) \int_0^\infty dR_\rho' \times u^*(v_\rho | R_\rho) V_\rho'(R_\rho', R_\rho) F_{\rho'}(v_\rho ', R_\rho'). \quad \rho \neq \rho',
\]

\[
\langle \nu_\alpha | D_\rho(R_\alpha) | \nu_\alpha^0 > = j(v_\alpha^0 | R_\alpha) \int_0^\infty dR u^*(v_\alpha | R) V_\rho'(R R_\alpha) u(v_\alpha^0 | R),
\]

\[
\langle \nu_\beta | E_\rho(R_\beta) | \nu_\alpha^0 > = u(v_\alpha^0 | R_\beta) \int_0^\infty dR u^*(v_\beta | R) V_\rho'(R_\beta, R) j(v_\alpha^0 | R),
\]

\[
\langle \nu_\rho | A_\rho'(R_\rho') | \nu_\rho > = -i u(v_\rho' | R_\rho) \int_0^\infty dR_\rho' \times u^*(v_\rho | R_\rho) V_\rho'(R_\rho', R_\rho) F_{\rho'}(v_\rho ', R_\rho'). \quad \rho \neq \rho',
\]

\[
\langle \nu_\alpha | D_\rho(R_\alpha) | \nu_\alpha^0 > = j(v_\alpha^0 | R_\alpha) \int_0^\infty dR u^*(v_\alpha | R) V_\rho'(R R_\alpha) u(v_\alpha^0 | R),
\]

\[
\langle \nu_\beta | E_\rho(R_\beta) | \nu_\alpha^0 > = u(v_\alpha^0 | R_\beta) \int_0^\infty dR u^*(v_\beta | R) V_\rho'(R_\beta, R) j(v_\alpha^0 | R),
\]

\[
\langle \nu_\rho | A_\rho'(R_\rho') | \nu_\rho > = -i u(v_\rho' | R_\rho) \int_0^\infty dR_\rho' \times u^*(v_\rho | R_\rho) V_\rho'(R_\rho', R_\rho) F_{\rho'}(v_\rho ', R_\rho'). \quad \rho \neq \rho',
\]

\[
\langle \nu_\alpha | D_\rho(R_\alpha) | \nu_\alpha^0 > = j(v_\alpha^0 | R_\alpha) \int_0^\infty dR u^*(v_\alpha | R) V_\rho'(R R_\alpha) u(v_\alpha^0 | R),
\]

\[
\langle \nu_\beta | E_\rho(R_\beta) | \nu_\alpha^0 > = u(v_\alpha^0 | R_\beta) \int_0^\infty dR u^*(v_\beta | R) V_\rho'(R_\beta, R) j(v_\alpha^0 | R),
\]
and consequently equation (3) takes the form
\[
\chi_\alpha (\nu_\alpha | R_\alpha ) = \sum I \langle \nu_\alpha | D_\alpha (R_\alpha ) | \nu_\alpha ^0 \rangle \langle \nu_\alpha | I_0^D | \nu_\alpha ^0 \rangle + \sum \sum I \langle \nu_\alpha | A_\alpha ^{\pi}(R_\alpha ) | \nu_\beta \rangle \langle \nu_\alpha | I_0^E | \nu_\beta \rangle,
\]
\[
\chi_\beta (\nu_\beta | R_\beta ) = \sum I \langle \nu_\beta | E_\beta (R_\beta ) | \nu_\alpha ^0 \rangle \langle \nu_\beta | I_0^E | \nu_\alpha ^0 \rangle + \sum \sum I \langle \nu_\beta | A_\beta ^{\pi}(R_\beta ) | \nu_\alpha \rangle \langle \nu_\beta | I_0^E | \nu_\alpha \rangle.
\]

Since \( \langle \nu_\rho | I_0^D | \nu_\rho ^0 \rangle \) and \( \langle \nu_\rho | I_0^E | \nu_\rho \rangle \) are independent of the form of the potential they can be determined explicitly:
\[
\langle \nu_\rho ^0 | I_0^E | \nu_\rho \rangle = ( - 1 )^{l + j + j'} M(l, j_\rho, j_\rho', J; l_\rho, l_\rho')
\]
and
\[
\langle \nu_\rho | I_0^D | \nu_\rho ^0 \rangle = ( - 1 )^{l + j + j'} M(l, j_\rho, l_\rho, J; j_\rho', l_\rho'),
\]
where
\[
M(l, j_\rho, a, J; b, l_\rho ) = [(2l_\rho + 1) \cdot (2j_\rho + 1)]^{1/2} C(l, j_\rho, a; 0, 0)
\]
\[
\times C(l, l_\rho, b; 0, 0) W(l, j_\rho, a, J; b, l_\rho).
\]
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It can be easily shown that

\[ \langle v_a | I_0^D | v_a^0 \rangle = \delta_{l_a,l_a^0} \delta_{j_a,j_a^0} \]

and substituting these \( \delta \) functions into (15) leads to a partial decoupling of the system of equations. However, it can easily be shown that only one subsystem possesses all inhomogeneous terms whereas the other ones do not have any terms of this kind and consequently their solutions are identically zero. The non-trivial solution exists therefore only for those \( \chi_a(v_a | R_a) \) functions that have \( j_a = j_{a0} \) and \( l_a = l_{a0} \) and for those \( \chi_\beta(v_\beta | R_\beta) \) that have \( j_\beta = l_{a0} \) and \( l_\beta = j_{a0} \), in other words:

\[
\begin{align*}
\chi_a(v_a | R_a) &\begin{cases} 
\neq 0 & \text{for } j_a = j_{a0}, l_a = l_{a0} \\
= 0 & \text{otherwise},
\end{cases} \\
\chi_\beta(v_\beta | R_\beta) &\begin{cases} 
\neq 0 & \text{for } j_\beta = l_{a0}, l_\beta = j_{a0} \\
= 0 & \text{otherwise}.
\end{cases}
\end{align*}
\]

(17)

From these equations we can immediately derive the corresponding relations for the \( T \) matrix elements. Recalling equation (4) we obtain

\[
\begin{align*}
(\text{non-reactive}) \tau(v_a | v_a^0) &\begin{cases} 
\neq 0 & \text{for } j_a = j_{a0}, l_a = l_{a0} \\
= 0 & \text{otherwise},
\end{cases} \\
(\text{reactive}) \tau(v_\beta | v_\beta^0) &\begin{cases} 
\neq 0 & \text{for } j_\beta = l_{a0}, l_\beta = j_{a0} \\
= 0 & \text{otherwise}.
\end{cases}
\end{align*}
\]

(18)

(19)

3.2. The anisotropic case

To study this case let us write equation (8) in the slightly different form

\[
V_\rho(R_a, R_\beta, \lambda) = \sum_{l=0}^{K_\rho_{\text{max}}} a_{l\rho} V_l^\rho(R_a, R_\beta) P_l(\cos \lambda),
\]

(8')

where \( \rho \) is either \( \alpha \) or \( \beta \).

The coefficients \( a_{l\rho} \) are measures of size of the corresponding potential terms and consequently all the \( V_l^\rho(R_a, R_\beta) \) are assumed to be of the same order of magnitude in the range of interest.

To make the analysis simpler it will be assumed that the potential is composed of two terms only and the generalization will be performed later. Thus:

\[
\begin{align*}
V_\alpha(R_\beta, R_a, \lambda) &= a_6^\alpha V_0^\alpha(R_\beta, R_a) + a_{i\rho}^\alpha V_i^\rho(R_\beta, R_a) P_i(\cos \lambda) \\
V_\beta(R_\alpha, R_\beta, \lambda) &= a_6^\beta V_0^\beta(R_\alpha, R_\beta) + a_{i\rho}^\beta V_i^\rho(R_\alpha, R_\beta) P_i(\cos \lambda).
\end{align*}
\]

(8'')
Consequently, when \( l \neq 0 \) and \( a_i \neq 0 \), the coupled system of integral equations takes the form

\[
\chi_\alpha(v_\alpha | R_\alpha) = a_0^\alpha \langle v_\alpha | D_0(R_\alpha) | v_\alpha^0 \rangle \langle v_\alpha | I_0^D | v_\alpha^0 \rangle + a_t^\alpha \langle v_\alpha | D_t(R_\alpha) | v_\alpha^0 \rangle \langle v_\alpha | I_t^D | v_\alpha^0 \rangle - a_0^\alpha \sum_{\nu_\alpha} \langle v_\alpha | A_0^\alpha(R_\alpha) | v_\beta \rangle \langle v_\alpha | I_0^E | v_\beta \rangle - a_t^\alpha \sum_{\nu_\alpha} \langle v_\alpha | A_t^\alpha(R_\alpha) | v_\beta \rangle \langle v_\alpha | I_t^E | v_\beta \rangle
\]

\[
\chi_\beta(v_\beta | R_\beta) = a_0^\beta \langle v_\beta | E_0(R_\beta) | v_\alpha^0 \rangle \langle v_\beta | I_0^E | v_\alpha^0 \rangle + a_t^\beta \langle v_\beta | E_t(R_\beta) | v_\alpha^0 \rangle \langle v_\beta | I_t^E | v_\alpha^0 \rangle - a_0^\beta \sum_{\nu_\alpha} \langle v_\beta | A_0^\beta(R_\beta) | v_\alpha \rangle \langle v_\beta | I_0^E | v_\alpha \rangle - a_t^\beta \sum_{\nu_\alpha} \langle v_\beta | A_t^\beta(R_\beta) | v_\alpha \rangle \langle v_\beta | I_t^E | v_\alpha \rangle
\]

(20)

To analyse these equations we have first to study the values of the inhomogeneous terms. All of them depend on the initial state \( |v_\alpha^0\rangle \) through the \( I^D \)s and the \( I^E \)s which obey the following rules:

\[
\langle v_\alpha | I_0^D | v_\alpha^0 \rangle \begin{cases} \neq 0 & l_\alpha = l_{\alpha_0} \; ; \; j_\alpha = j_{\alpha_0} , \\ = 0 & \text{otherwise,} \end{cases}
\]

\[
\langle v_\alpha | I_t^D | v_\alpha^0 \rangle \begin{cases} \neq 0 & |l_\alpha - l| \leq l_\alpha \leq l_{\alpha_0} + l ; \; |j_\alpha - j| \leq j_\alpha \leq j_{\alpha_0} + j ; \\ 0 & \text{otherwise,} \end{cases}
\]

\[
\langle v_\beta | I_0^E | v_\alpha^0 \rangle \begin{cases} \neq 0 & l_\beta = j_{\beta_0} , \; j_\alpha = l_\alpha , \\ = 0 & \text{otherwise,} \end{cases}
\]

\[
\langle v_\beta | I_t^E | v_\alpha^0 \rangle \begin{cases} \neq 0 & |l_\alpha - l| \leq j_\beta \leq l_{\alpha_0} + l ; \; |j_\alpha - j| < l_\beta < j_{\alpha_0} + l ; \\ 0 & \text{otherwise.} \end{cases}
\]
If the inhomogeneous term in equation (20) are taken to be the zero approximation to the exact solution (the Born Approximation) then, recalling equation (4), one notices that the corresponding $\tau$ matrix element is linearly proportional to the respective $a_t$. Thus the larger the value of $a_t$ (which means a relatively larger contribution of the $l$th term in the potential expansion) the larger will be the expected transition probability. If, on the other hand, a given state is outside the 'l range', its zero approximation to the transition probability is zero (because the respective inhomogeneous term in the equations is zero) and consequently the $\tau$ matrix element will be proportional to a product of $a_t$'s which in general results in a weaker transition, because in most physical cases a product of two $a_t$'s is smaller than each $a_t$.

The generalization to the case where more than two terms are included in the potential expression is straightforward and therefore does not need more consideration.

4. DISCUSSION

In the analysis performed in the last section we have shown that in a two-channel problem where one mass is infinitely heavy, one can get significant information on the distribution of rotational states of products by considering the terms in the expansion of the potential in Legendre polynomials.

For a given initial state specified by the pair of rotational quantum numbers $(j_0, l_0)$, two sets of rotational quantum numbers $\{j'_0, \ldots, j'_n\}$ and $\{j_0', \ldots, j_0''\}$ can be generated. The first set contains the states to which a rotational transition might occur due to an inelastic collision, whereas the second contains those to which a rotational transition might occur in case of an exchange interaction. It was found that the $\alpha$ set contains the initial state $j_0$ (and not necessarily a state corresponding to $l_0$) and, in general, states specified by rotational numbers in the vicinity of $j_0$. The $\beta$ set contains a state specified by the number $l_0$ and, in general, the other numbers in the set are in the vicinity of $l_0$.

In order to predict if a given transition is expected to be of importance or not, one has to find $l(\alpha) = |j_0 - j'_0|$ in case of an inelastic transition or $l(\beta) = |j_0 - j_0'|$ in case of a reactive one. Having these numbers and assuming the expansion of the potential in terms of Legendre polynomials is known, the next step is to see whether $l(\rho)$ (where $\rho$ stands for either $\alpha$ or $\beta$) is larger than $l(\rho)_{\text{max}}$ where $l(\rho)_{\text{max}}$ is the largest $l$ in the expansion. In case $l(\rho) > l(\rho)_{\text{max}}$, the respective transition is expected to be of relatively low significance. The same holds if $l(\rho) < l(\rho)_{\text{max}}$, but the various $l$'s for which $l(\rho) < l$ correspond to $a_t$'s of relatively small values. If, on the other hand, $l(\rho) < l(\rho)_{\text{max}}$, and there exists at least one $l$ for which $l > l(\rho)$, and the corresponding $a_l$ is relatively large, then the transition is expected to be of a relatively high probability.

In general, one would expect the expansion to be only of a few terms and consequently the sets $\{j_0\}$ and $\{j_0\}$ would be small (but around $j_0$ and $l_0$, respectively).

In case the potential is angular independent (the isotropic case), a stronger argument can be made. It turns out that once the molecular internal rotational quantum number $j_0$ and the orbital quantum number $l_0$ of reagents are specified, the rotational quantum numbers of the final products are uniquely determined. It was proved that in the inelastic channel no rotational transitions occur,
whereas in the reactive one the new molecule is formed in a single rotational state with the rotational quantum number \( j = j_0 \).

Similar results, although less restrictive, are expected in a system \( BC + A \rightarrow AB + C \) where \( B \) is relatively heavy but finite. An example of such a two-channel system is the \((HF + Li)\) system\(^\dagger\). Here, \( m_F \gg m_{Li}, m_H \) and the possibility of forming the product \( LiH \) is highly unfavoured because of the high endothermicity of the reaction \( HF + Li \rightarrow LiH + F \).

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**References**


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