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TOPICAL REVIEW

Rotational rainbow effects in electron–molecule and atom–molecule scattering

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Abstract. Rotational rainbow structures in atom/electron–molecule scattering are analysed by means of simple dynamical approximations as hard-shell molecules, the infinite order sudden (IOS) approximation and the $N$-centre spectator model. Typical collision systems described are atom–molecule scattering for collision energies of $10^{-1}$ eV and electron–molecule scattering at $10^2$ eV. The IOS and spectator rotational rainbow patterns are compared and special features related to initially excited molecules, $m$-changing collisions, multiple rainbows, and inversion techniques are discussed. The rotational rainbow patterns for polyatomic molecules (symmetric tops) are discussed as well as vibrational effects in the rotational rainbow structures of diatomics.

1. Introduction

Rotational transitions in scattering of anisotropic, non-spherical systems are of interest in many branches of physics, ranging from nuclear to astrophysics. Here we will discuss molecular collisions as a prototype, as for instance the collision of an atom or electron A with a diatomic molecule BC. During the last two decades it has been realized that the longstanding folklore of ‘small rotational transitions in a single encounter’ was wrong. In an increasing number of cases very large rotational momentum changes are observed and quite often these processes occur with high probability.

In addition a fundamentally new scattering phenomenon was found, which had not been anticipated before, namely the so-called rotational rainbows. These effects are named ‘rainbows’ because of their close analogy to the rainbows appearing in scattering for isotropic potentials. It should be stressed, however, that these potential scattering rainbows are due to attractive wells (or at least points of inflection [1]) in the radial potential, whereas the rotational rainbows are a consequence of the anisotropy of the potential. For a more general discussion of rainbow catastrophes in atomic and molecular collisions see, e.g., [2, 3].

Rotational rainbows are prominent features in the rotationally inelastic differential cross sections. As typical examples from nuclear and molecular scattering figures 1–3 show the transition probabilities from the rotational ground state at a fixed scattering angle $\theta$ in the centre-of-mass frame. Figure 1 has been obtained for Coulomb excitation of $^{238}$U colliding with $^{84}$Kr at an energy of 300 MeV [4], figure 2 for He–Na$_2$ collisions at 100 meV [5], and figure 3 for electron–Na$_2$ at an impact energy of 300 eV [6]. Apart from subtle differences the three distributions appear to be quite similar: the quantum distributions show a pronounced maximum (the ‘rotational rainbow’)
at a slightly smaller value of the rotational quantum number than the singularity of the classical distributions, which is also shown in figures 2 and 3. On the classically allowed side of the rainbow quantum oscillations appear, the so-called rotational rainbow oscillations. It should be noted that in all cases only even transitions are allowed because of the symmetry of the targets. More about rotational rainbows in heavy ion collisions can be found in the original articles [4, 7–9] and in the more recent review on inelastic nuclear scattering by Landowne and Vitturi [10].

Rotational rainbows in atom–molecule collisions have been extensively studied since their first appearance in the literature (some early examples are the impulsive spectator model studied by one of the authors [11], the classical trajectory computations by Thomas [12] and the hard-shell model studied by Beck [13–15] and by Bosanac [16]). Rotational rainbows have been observed experimentally for many systems in state-to-state differential cross sections (see, e.g., the overviews by Beck [15], Faubel [17], Toennies [18], Buck [19]). As an example figure 4 shows measured Ne–Na₂ cross sections [20] in the laboratory frame at a collision energy of 190 meV in excellent agreement with theoretical results [20]. Here the rotational rainbows appear in the angular distribution as discussed below. More recent results at higher collision energy have been reported for Na⁺ colliding with N₂ or CO at about 100 eV [21, 22]. The theoretical description of rotational rainbow structures has been discussed in detail in the review articles by Dickinson and Richards [23] or Schinke and Bowman [24], which are largely based on the infinite-order sudden (IOS) approximation in combination with a semiclassical analysis. This is discussed in more detail in section 2.1.1.

More recently—and again quite unexpectedly—very pronounced rotational rainbow structures have been observed experimentally and described theoretically in electron–molecule collisions at intermediate energies [25–28]. In fact, these rainbow structures are even more pronounced than those found before. This is mainly...
due to the extreme anisotropy of the interaction, which on the other hand makes a treatment within the framework of the 10s approximation impossible. A very satisfactory description is, however, given by the impulsive spectator model (also called N-centre scattering model), which is discussed in section 2.1.2.

Rotational rainbow structures have also been observed in molecule–surface scattering [29–31] in photodissociation [32–35], as well as in dissociative ion–molecule processes [36] and they appear to be quite common phenomena.

In the present article we will discuss the theoretical description of rotational rainbow structures in direct atom/electron–molecule collisions under sudden conditions. We emphasize simple dynamical approximations, like the 10s approximation, hard-shell molecules and the N-centre spectator model, which are sometimes amazingly
In this section we will discuss the rotational rainbows for by far the most extensively studied case, namely the collision of a particle, e.g. an atom or an electron, with a diatomic molecule or, somewhat more general, a linear molecule like CO$_2$. In the following it is assumed in addition that the molecule is rigid, i.e. it can only rotate in space as a whole and does not possess internal degrees of freedom. Vibrational internal motion, vibrationally inelastic transitions and the induced modification of the cross sections for rotational transitions are discussed in section 4.

Needless to note that we do not consider in any detail the electronic degrees of freedom, i.e. the collision process is entirely described by an anisotropic potential $V(R, \gamma)$ depending on the distance, $R$, between the particle and the molecular centre-of-mass and the angle, $\gamma$, between $R$ and the molecular axis. In many applications the potential is expanded in terms of Legendre polynomials

$$V(R, \gamma) = \sum_k V_k(R) P_k(\cos \gamma).$$

We are furthermore interested here in systems with strong rotational coupling. In particular we assume sudden conditions (short collision time) and almost energetically elastic collisions (energy transfer small compared to the kinetic collision energy). In the main part of this section we also restrict ourselves to purely repulsive or attractive interactions and symmetric molecules, as for instance homonuclear diatomics. Some remarks on the modifications of rotational rainbow structures for interaction potentials with both attraction and repulsion as well as for heteronuclear molecules can be found in section 2.4, the effects of multiple collisions are addressed in section 2.4.3.

One of the most simple models for investigating rotationally inelastic transitions is the scattering from a rotationally symmetric rigid shell described by a curve $R(\gamma)$, for example a hard ellipsoid. In classical mechanics such rigid shell scattering has been quite extensively studied [37–42], for quantum results see [48–50].

The model allows a very helpful insight into the basic mechanism underlying the formation of rotational rainbows: conservation of linear and angular momentum directly leads to the simple, however very useful, equation for the change of the
molecular rotational momentum $J$ (throughout this paper classical angular momenta are divided by $\hbar$ and therefore dimensionless and instead of the linear momentum, $p = \sqrt{2\mu E}$, we use the wavenumber $k = p/\hbar$)

$$\Delta J = R \times \Delta k = \Delta k R \times n(R). \quad (2)$$

Here $R$ denotes the point of contact on the rigid shell, $n$ is the normal unit vector at this point and the momentum transfer is under energetically sudden conditions $|k'| \approx |k| = k$ given by

$$\Delta k = |\Delta k| = |k' - k| \approx 2k \sin \vartheta/2 \quad (3)$$

where $\vartheta$ is the scattering angle. The absolute value of the rotational momentum transfer $2$ depends on the orientation of the molecular axis and can vary between zero and a maximum accessible value. In a good approximation the maximum final rotational momentum (assuming an initially non-rotating molecule) at a scattering angle $\vartheta$ is given by

$$J_R = \hat{J} \sin \vartheta/2 \quad (4)$$

where $\hat{J}$ is the overall maximum of the rotational momentum transfer, which is found for backward scattering.

For the case of a hard ellipsoid with long half-axis $a$ and small half-axis $b$ one obtains approximately $[51]$

$$\hat{J} = 2k(a - b) \quad (5)$$

which is proportional to the collision velocity and to the anisotropy of the interaction.
The rigid shell model can be used for straightforward numerically exact classical computations. The same can be done for classical scattering from non-rigid potentials, it is however, much less efficient because of the need to solve the equations of motion instead of tracing straight line trajectories. The classical and semiclassical excitation probabilities for $^{84}\text{Kr} + ^{238}\text{U}$ collisions at 385 MeV are given in figure 5 [9, 10]. Similar results have been obtained for molecular systems at about the same time, as shown in figure 6 for He–Na$_2$ collisions at 100 meV [52], where exact classical trajectory computations are compared with approximate ones (classical 10s approximation as discussed below).

![Figure 6](image-url)

**Figure 6.** Exact classical (histogram) and classical 10s differential cross sections for rotational transition $0 \rightarrow j = 4$ and $j = 14$ for He–Na$_2$ collisions at 100 meV. (Adapted from [52].)

In quantum mechanics a full numerical solution is, in most cases, beyond the present computational feasibility because of the large number of channels. Therefore one has to rely on approximations. For weak coupling, perturbative methods such as the distorted wave approximation can be used. In the strong coupling regime one can try to develop approximations which simplify the dynamics of the system drastically. Two of these dynamical approximations are discussed in the following.

### 2.1. Dynamical approximations

#### 2.1.1. Infinite-order sudden approximation (10s).

One of the most successful dynamical approximations for rotationally inelastic transitions in the strong coupling regime is the so-called infinite-order sudden (10s) approximation [53], which achieves a complete decoupling of the translational and rotational degrees of motion. The 10s approximation is based on two assumptions: the energy sudden approximation (= no energy transfer) and the centrifugal sudden approximation (an effective orbital angular momentum is conserved during the collision). The last assumption is typically the most important one, the first one can be weakened or omitted, leading to a variety of so-called ‘coupled-state’ approximations. Clearly the centrifugal sudden approximation assumes that the anisotropy of the potential is only small (note that this does not imply weak rotational transitions). For a recent discussion of the validity of the sudden conditions see Nakamura [54].
Here we give a short resume of the quantum 10s approximation. The same dynamical assumptions can be used for decoupling the classical equations of motion (see, e.g., [52]). Here we confine ourselves to the case $j_{\text{initial}} = 0$. The influence of an initial rotation is discussed in section 2.2. The theoretical derivation of the 10s approximation has been described in detail [53]. Here we only give the working equations for the differential state-to-state cross sections, which are the basis for the semiclassical analysis (see also the review by Schinke and Bowman [24]):

$$\frac{d\sigma}{d\Omega} (j \rightarrow 0|\theta) = \left| \frac{1}{2i k} \sum_{\ell=0}^{\infty} (2\ell + 1) P_{\ell} (\cos \theta) T_{\ell} (j \rightarrow 0) \right|^2$$

(6)

with a transition amplitude given by

$$T_{\ell} (j \rightarrow 0) = \sqrt{2j + 1} \int_0^{\pi/2} d\gamma \sin \gamma \left\{ e^{2i\delta_\ell (\gamma)} - 1 \right\} P_j (\cos \gamma).$$

(7)

The potential enters only via the phases $\delta_\ell (\gamma)$, which are precisely the elastic scattering phase shifts for potential scattering from a potential $V(R, \gamma)$, where the orientation angle $\gamma$ is treated as a fixed parameter. Note that the 10s approximation averages over contributions from all orientations of the molecule. Note also that the upper limit of the integration, $\pi/2$, can be chosen because of the symmetry of the potential, $V(R, \pi - \gamma) = V(R, \gamma)$. Hence (6) is only valid for even $j$. Transitions to odd $j$-values are forbidden. In (6) and (7) only rotational transitions are resolved, the transitions to the $(2j + 1)$ magnetic sublevels, $m$, are summed. A more detailed discussion of $m$-changing collisions can be found in section 2.3.

In many cases a semiclassical version of the 10s approximation [5, 24] has been found to be very helpful for analysing the various features of the cross sections, simplifying numerical computations and, last but not least, for developing inversion methods (see section 2.5). The most straightforward derivation of the semiclassical 10s approximation starts from the quantum equations above following essentially the same steps as in the semiclassical analysis of elastic potential scattering, i.e. sums are converted to integrals by means of the Poisson summation formula, the integrand is approximated semiclassically (WKB phase shifts, asymptotic expressions for the Legendre polynomials), the integrals are evaluated by means of the stationary phase analysis, the resulting integrals are summed over the magnetic sublevels, $m$, by means of uniformization.

The stationary phase conditions

$$\Theta(L, \gamma) = \pi - 2L \int_{R_0}^{R} \frac{dR}{R^2 \sqrt{k^2 - v(R, \gamma) - L^2/R^2}} = \mp \delta$$

(8)

$$J(L, \gamma) = - \int_{R_0}^{\infty} \frac{\partial v}{\partial \gamma} \frac{dR}{\sqrt{k^2 - v(R, \gamma) - L^2/R^2}} = j + \frac{1}{2}$$

(9)

with $v(R, \gamma) = 2mV(R, \gamma)/\hbar^2$, generate the classical expressions for the deflection function $\Theta(L, \gamma)$ and the rotational excitation function $J(L, \gamma)$. All solutions
Topical review

$(L_\nu, \gamma_\nu)$ of the stationarity conditions must be summed, i.e. one has to superimpose all contributing classical trajectories. Assuming two such contributions, $\nu = 1, 2$, the final (primitive) semiclassical result is

$$\frac{d\sigma}{d\Omega}(j \leftarrow 0|\theta) = \frac{2}{k^2 \sin \theta} \left[ F_1^2 + F_2^2 + 2F_1F_2 \sin(\Phi_1 - \Phi_2) \right]$$

(10)

with

$$F_\nu = \left\{ \frac{1}{L_\nu \sin \gamma_\nu} \left| \frac{\partial(\Theta, J)}{\partial(L, \gamma)} \right|_\nu \right\}^{-1/2}.$$  

(11)

Here

$$\Phi_\nu = 2\delta(L_\nu, \gamma_\nu) - \theta L_\nu - J \gamma_\nu$$

(12)

is the classical collision action along the trajectory and $\delta(L, \gamma)$ is the WKB expression for the phase shift $\delta_\nu(\gamma)$. When the interference term in (10) is omitted the classical cross section is obtained which can also be derived from a purely classical version of the 10s approximation [52].

The classical and the primitive semiclassical cross sections diverge at the classical rotational rainbow, which appears at the critical points of the dynamical mapping $(L, \gamma) \leftrightarrow (\Theta, J)$ determined by the vanishing of the Jacobian

$$\left| \frac{\partial(\Theta, J)}{\partial(L, \gamma)} \right|_R = 0$$

(13)

which is the rainbow condition determining the critical values (the rainbows) written as $J_R = J_R(\theta)$ or $\theta_R = \theta_R(J)$. Within a good approximation one finds $J_R = \bar{J} \sin \theta / 2$ as in (4), where $\bar{J}$ is proportional to the wavenumber $k$. A typical situation is shown in figure 7 for He–Na$_2$ scattering at 0.1 eV (adapted from [24]). In the central part we see the rotational rainbow curve, related to the extremum of the classical excitation function shown in the upper right corner (quantum number $j$ and classical rotational momentum $J$ are semiclassically related by $J = j + \frac{1}{2}$). On the bright side of the classical rainbow we have two contributing classical trajectories leading to an interference pattern in quantum mechanics, which is observable both in the differential state-to-state cross sections as a function of the scattering angle $\theta$ or in the population of the final rotational states $j$ at a fixed value of $\theta$.

The region outside the rainbow curve is classically forbidden. Transitions into this region can be described semiclassically by a complex-valued extension of classical dynamics. In addition a uniform semiclassical approximation [5] avoids the rainbow singularity and typically agrees very well with quantum results.

The most prominent feature of the rotationally inelastic cross sections is the first rotational rainbow maximum, which is shifted from the classical rainbow singularity into the classically allowed region. More of these rotational rainbow oscillations ('supernumerary rainbows') appear at lower values of $j$ or larger values of $\theta$, respectively. The uniform semiclassical analysis [5] leads to the following rules, which are of practical importance.
Figure 7. Classical rotational rainbow curves $j_R(\theta)$, the location of the first rotational rainbow maximum $j_{R,\text{max}}(\theta)$, the classical excitation function $j(L, \gamma)$ and IOS differential excitation probabilities $P(j \leftarrow 0|\psi)$ as a function of $\psi$ as well as $j$. The collision system is He–Na$_2$ at a collision energy of 0.1 eV. (Adapted from Schinke and Bowman [24].)

(i) The value of the cross sections at the classical rainbow is about 44% of the value at the first maximum.

(ii) The position of the $i$th maximum is approximately given by [5, 55, 56]

$$j_{i,\text{max}}^\text{max} = J_R - \frac{1}{2} - \xi_i (2J_R)^{1/3}$$

where the $\xi_i$ are the negative positions of the extrema of the Airy function, i.e. 1.019, 3.248, 4.820, ... [57]. A similar equation applies to the oscillations of the differential cross sections as function of the scattering angle $\theta$.

(iii) In particular the distance between the rainbow position and the first maximum satisfies

$$(J_R - j_{1,\text{max}}^\text{max} - \frac{1}{2}) J_R^{-1/3} = \xi_1 2^{1/3} = 1.284$$

(note the difference between this value and the result (28) from the spectator model).

The IOS approximation is based on the assumption of a weak or modest anisotropy of the interaction potential. Typical values of the anisotropy, e.g., the relative difference of the classical turning points for head-on, $\gamma = 0^\circ$, and perpendicular, $\gamma = 90^\circ$ orientations, are found to be about 0.2. Under such weak anisotropy conditions the IOS approximation can be furthermore simplified by separation of the cross sections into a $j$-independent part—the total differential cross section—times a probability for rotational transitions [58–60]:

$$\frac{d\sigma}{d\Omega} (j \leftarrow 0|\psi) = \frac{d\sigma}{d\Omega} (\theta) P_{\ell(\psi)}(j \leftarrow 0)$$

and

$$P_{\ell(\psi)}(j \leftarrow 0) = \left| T_{\ell(\psi)}(j \leftarrow 0) \right|^2$$
where $\ell(\theta) = L(\Theta) - \frac{1}{2}$ is the partial wave belonging to the classical angular momentum $L$ leading to a deflection angle $\Theta$. The overall scattering cross section $d\sigma/d\Omega(\theta)$ is computed as elastic scattering from an effective spherically symmetric potential, e.g. the zero-order term in expansion (1). A further semiclassical approximation finally leads to

$$T'(j+0) = \frac{1}{j+1} \sqrt{2j+1} \int_0^\pi d\gamma \sin \gamma e^{2i\delta^{(s)}(\gamma)} P_j(\cos \gamma)$$

where $\delta^{(s)}(\gamma)$ is the anisotropic part of the semiclassical phase shift (compare the similar factorization of the cross sections in the spectator model below).

The classical version of the IO5 approximation has been used to test the validity of the dynamical approximation scheme in comparison with exact classical trajectory computations [52, 61]. The reported good agreement (an example is shown in figure 6) was accompanied by the observation of characteristic structural deviations: the square root rainbow singularity is changed into a logarithmic singularity plus a step at the boundary of the allowed region. In addition a less pronounced second logarithmic singularity appears for small values of $j$. These findings are in accord with purely theoretical considerations [40] and are also observable in heavy ion scattering (compare figure 5).

2.1.2. Spectator model. The spectator model is based on the usual assumptions of the impulse approximation.

(i) The collision is sudden (impulsive), i.e. the interaction time between the incoming particle and the target is short compared to typical vibrational or rotational periods of the target.

(ii) The interaction potential is approximated by a superposition of pair potentials.

(iii) The scattering amplitude is approximated by a superposition of scattering amplitudes of the target constituents. Multiple collisions and screening effects are neglected.

More details of the impulse approximation are given in the recent reviews [62, 63] or in the original papers involving the first of the authors [11, 64-68]. As an example for one of the earliest appearances of rotational rainbows in molecular scattering figure 8 shows results published in 1974 for a simplified dumb-bell model of $\text{Li}^+-\text{N}_2$ collisions at a collision energy of 1 eV [11]. Note that the molecule is not assumed to be rigid in this model and therefore it can also undergo vibrational excitations. The figure shows differential state-to-state cross sections at a fixed scattering angle of $\theta = 150^\circ$ for rotational and vibrational transitions out of the ground state as a function of the energy transfer (note the high amount of energy transfer in this example compared to the other systems discussed here). The vibrational transitions will be considered in section 4 but the vibrationally elastic, rotationally inelastic cross sections clearly show the rotational rainbow features. The model had, however, the disadvantage that its anisotropy was much too large compared to the realistic collision system at this energy region and therefore the studies reported in [11] and in subsequent articles [64-68] could only be considered as model studies. Recently the situation has changed quite unexpectedly for the case of electron–molecule scattering at impact energies of about $10^2$ eV, where all of the conditions of the impulsive model
An early example (impulsive spectator model) of rotational rainbows in molecular collisions. Differential cross sections for rotational vibrational transitions 0, 0 → j, n for Li⁺-N₂ collisions at 1 eV for scattering angle θ = 150° as a function of the energy transfer ΔE. The arrows mark the classical rainbow positions. (Adapted from [5].)

are satisfied. An additional simplification can be achieved in this case by neglecting the energy transfer.

If $\hat{T}$ is the transition operator in the centre of mass for the scattering of an electron by a single target atom, the transition operator for the atom shifted by the displacement operators [69, 70] $D(d) = \exp(-i d \cdot k)$ and $D'(d) = \exp(-i d' \cdot k')$ (with the position vector, $d$, of the atom from the centre of mass of the target molecule and the initial and final wavenumbers $k$ and $k'$) is given by

$$T = D'(-d) \hat{T} D(d). \quad (19)$$

For homonuclear molecules the transition matrix elements between asymptotic rotor states $|jm_j k\rangle$ ($j = \text{rotational quantum number}, m = \text{projection quantum number onto a prescribed axis}$) factorize into a molecular form factor

$$F_{j,m'j,m} = \langle j' m' | e^{i \Delta \cos \theta} + e^{-i \Delta \cos \theta} | j m \rangle \quad (20)$$

and the scattering amplitude $f(\theta) = \langle k' | \hat{T} | k \rangle$. In (20) the contributions from the two constituents of the diatomic molecule are summed. The molecular anisotropy enters via the parameter

$$\Delta = d \Delta k \quad (21)$$

where $d$ is the distance of the two atoms from the centre of mass, i.e. half of the equilibrium distance $r$, and $\Delta k = k' - k$ the momentum transfer which is given under energetically sudden conditions $|k'| \approx |k| = k$ by (3). The angle between the position vector $d_1$ of one of the molecular atoms and $\Delta k$ is denoted by $\theta$.

In the following we specify transitions from the rotational ground state and drop the prime of the final rotational quantum number. For initially excited states we refer to section 2.2.
Choosing the quantization axis in the direction of $\Delta k$ (kinematic apse) the form factor takes the simple form

$$F_{jm00} = \delta_{m0} F_{j000} \quad \text{with} \quad F_{j000} = 2 S_j^2 \sqrt{2j + 1} i^j j_j(\Delta)$$

(22)

where $j_j$ is the spherical Bessel function. The selection rule $\Delta j = j = \text{even}$ is given by the factor

$$S_j^2 = \frac{1}{2} \left[ 1 + (-1)^j \right]$$

(23)

and the differential cross section is given by

$$\frac{d\sigma}{d\Omega}(j \leftarrow 0|\vartheta) = |F_{j000}|^2 \left( \frac{d\sigma}{d\Omega} \right)_{\text{atom}}$$

(24)

where $(d\sigma/d\Omega)_{\text{atom}} = |f(\vartheta)|^2$ is the cross section of the electron–atom scattering. In the spectator model of homonuclear diatomics the transition probabilities are given by

$$P(j \leftarrow 0|\vartheta) \approx \frac{1}{2} |F_{j000}|^2 = 2 S_j^2 (2j + 1) j_j^2(\Delta)$$

$$= \begin{cases} 2(2j + 1) j_j^2(\Delta) & j \text{ even} \\
0 & j \text{ odd} \end{cases}$$

(25)

for $\Delta = rk \sin \vartheta/2 \gg 1$.

In figure 3 the results of spectator model (25) are compared with the results of close coupling computations. The classical rotational rainbow, which is also plotted in figure 3, is given by [6, 71]

$$P_C(J \leftarrow 0|\vartheta) = \frac{2J}{J_R \sqrt{J_R^2 - J^2}}$$

(26)

with $J = j + \frac{1}{2}$. The maximum final rotational momentum is given by (4) with the overall maximum in the spectator model, $J = rk$. The classical distribution shows the well known square root divergence at the classical rainbow. On the classically allowed side of the rainbow the quantum results oscillate around the classical curve and show a pronounced maximum just below the classical singularity. An exponential decrease in the spectator results is observable for increasing $J$ on the classical forbidden side. The quantum mechanical behaviour is well understood by a semiclassical approximation to (25). Furthermore the classical limit leads to the probability (26) with $\Delta = J_R$ and $\Delta_m := \Delta(\pi) = \tilde{J}$, where a factor two appears automatically as a result of the selection rule $\Delta j = \text{even}$. Note the following useful rules.

(i) The value of the cross sections at the classical rainbow is about 44% of the value at the first maximum.

(ii) The position of the $i$th maximum is given by [5, 55, 56]

$$J_i^{\text{max}} = J_R - \frac{1}{2} - \xi_i(J_R/2)^{1/3}$$

(27)
where the $\xi_i$ are the negative positions of the extrema of the Airy function, i.e. 1.019, 3.248, 4.820, ...[57] (note the difference from (14)). A similar equation applies to the oscillations of the differential cross sections as function of the scattering angle $\vartheta$.

(iii) The distance between the rainbow position and the first rotational rainbow maximum satisfies

$$(J_R - J_1^{\text{max}} - \frac{1}{2})J_R^{-1/3} = \xi_1 2^{-1/3} = 0.809$$

which value is noticeably different from the corresponding 10S result (15).

Figure 9 shows transition probabilities, $P(j \rightarrow 0|\vartheta)$, calculated by the spectator model as a function of the final $j$ and the scattering angle, $\vartheta$, for a fixed maximal value of $\Delta$ by $\Delta_m = 25$. The three-dimensional plot in figure 9(a), which is a representation similar to figure 3, is shown as a contour plot in figure 9(b). The classical rainbow (26) is also shown for comparison in figure 9(b). The transition probabilities from the spectator model form a chain of maxima along the classical rainbow. The height of these decreases for increasing scattering angle. The selection rule $\Delta j = j = \text{even}$ for non-vanishing cross section splits this mountain range into a series of peaks. On the allowed side of the classical rainbow the distribution shows an oscillatory pattern and, on the other, an exponential fall off.

![Figure 9](image_url)

**Figure 9.** Rotational transition probabilities, $P(j \rightarrow 0|\vartheta)$, for electron-diatom scattering ($\Delta_m = 25$) as a function of $\vartheta$ and $j$. 
Note that the spectator model is not restricted to homonuclear molecules. Differential cross sections for heteronuclear diatomic molecules are discussed in [6].

2.1.3. Comparison of IOs and spectator rainbow structures. The rotational rainbow structures discussed earlier within the IOs approximation and the spectator model are very similar. This is particularly evident in a comparison of the simplified IOs equations (16)–(18) with the equivalent formulae (24)–(25) of the spectator model. An equivalent to the IOs equation (18) can be found from the integral representation of the Bessel function [57]

\[ j_j(\Delta) = \frac{1}{2}(-1)^j \int_0^\pi d\gamma \sin \gamma e^{i \Delta \cos \gamma} P_j(\cos \gamma) \]  

(29)

where the IOs anisotropic phase shift \( 2\delta_k(\gamma) \) is replaced by the phase difference \( \Delta \cos \gamma = rk \cos \gamma \sin \vartheta/2 \) due to the shift of the scattering centres from the centre of mass.

Despite the overall similarity one should be aware of important differences. First, the IOs approximation assumes small anisotropy and the resulting overall differential cross section \( d\sigma/d\Omega \) is the differential cross section for scattering from the molecule as a whole, whereas in the spectator model an extremely anisotropic dumbbell molecule is considered and \( d\sigma/d\Omega \) is the cross section for elastic scattering from one of the molecular atoms.

The skeleton of the rotational rainbow structure is the same. In both cases we find a \( J_R = J \sin \vartheta/2 \) angular dependence of the classical rainbow singularity, where \( J \) is proportional to \( k \), and the same 44% ratio between the height of the first rainbow maximum and the quantum cross section at the classical rainbow. The positions of the rotational rainbow maxima are, however, markedly different, as seen from (14) and (27). In particular the ratios for the first rainbow maximum specified in (15) and (28) differ by a factor of 1.6. Another difference manifests itself in the low-\( j \) behaviour, where the spectator model leads to a vanishing transition probability \( P(J \leftarrow 0|\vartheta) \sim J \) in the classical limit (compare (26)) and the IOs cross section remains finite, showing typically a behaviour like

\[ P_C(J \leftarrow 0|\vartheta) \sim \frac{1 + cJ}{\sqrt{J_R - J}} \]  

(30)

with a constant \( c \). This is also visible in the oscillatory quantum rainbow patterns shown in figures 2 and 3, where the electron–molecule cross sections decay much faster towards smaller values of \( j \). This difference in the low-\( J \) behaviour leads to different singularity structures for the classical cross sections for initially rotating molecules as discussed in the following section.

These differences can be easily used to distinguish between an IOs or spectator type of collision for any observed rotational probability distribution.
2.2. Transitions out of excited states

In the preceding sections we have confined ourselves to molecules initially in the rotational ground state. The influence of initial excitation has been studied by a number of authors [6, 14, 59, 67, 72].

In most experiments the \( m \) substates are not resolved and one is interested in cross sections which are averaged over initial and summed over final \( m \) substates, i.e.

\[
\frac{d\sigma}{d\Omega}(j' \leftarrow j|\vartheta) = \frac{1}{2j + 1} \sum_{m'm} \frac{d\sigma}{d\Omega}(j'm' \leftarrow jm|\vartheta)
\]

(31)

which is independent of the quantization axis. Any convenient axis can be chosen.

In some important cases one can derive relations which directly relate the cross sections for initially excited targets to those for transitions out of the ground state. Such so-called factorization or scaling relations are well known for rotational transitions of linear rigid rotors under sudden conditions [53, 73, 74] (for a discussion of other molecular collision systems see [75-77]). This factorization relation follows from the factorization of the \( T \)-matrix elements in IOT theories and of the form factors in the spectator model. The derivation is immediate in the spectator model [6, 11, 25] starting from (20) and adopting the kinematic apex \( \Delta k \) as quantization axis. A few algebraic manipulations lead to

\[
F_{j'm'jm} = \sum_{j''} C^{j''0}_{j'm'jm} F_{j''000}
\]

(32)

where \( F_{j''000} \) is the form factor (22) for the transition out of the ground state and the coefficients

\[
C^{j''m''}_{j'm'jm} = (-1)^{m'} \sqrt{(2j' + 1)(2j'' + 1)(2j + 1)} \begin{pmatrix} j' & j'' & j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & j'' & j \\ -m' & m'' & m \end{pmatrix}
\]

(33)

are algebraic quantities independent of the system parameters. The amplitudes \( F_{j'm'jm} \) in (32) satisfy the selection rule \( m' = m \) as a consequence of the chosen quantization axis. Inserting

\[
\frac{d\sigma}{d\Omega}(j'm' \leftarrow jm|\vartheta) = |F_{j'm'jm}|^2 \frac{d\sigma}{d\Omega} \text{atom}
\]

(34)

into (31) yields the celebrated factorization formula

\[
P(j' \leftarrow j|\vartheta) = \sum_{j''=|j'-j|}^{j'+j} C_{j''j'} j P(j'' \leftarrow 0|\vartheta)
\]

(35)

with weight coefficients

\[
C_{j''j'}j = (2j' + 1) \begin{pmatrix} j' & j'' & j \\ 0 & 0 & 0 \end{pmatrix}^2
\]

(36)
for rotational transition probabilities out of excited states. The same factorization formula is valid for differential and integral state-to-state cross sections and also for collision rates [53].

The mechanism underlying the factorization relation is the fact that the essential part of the collision dynamics is independent of the initial state of the target, which enters only in a probabilistic way by the statistical weight factors (36). This is most clearly demonstrated in the classical version of the factorization equation [6, 78]

$$P_C(J' \rightarrow J|\vartheta) = \int_{J'-J}^{J'+J} \frac{8J'P_C(J'' \rightarrow 0|\vartheta) dJ''}{\pi \sqrt{[(J' + J)^2 - J''^2][J''^2 - (J' - J)^2]}}.$$  

(37)

The classical excitation probability $P_C(J'' \rightarrow 0|\vartheta)$ for transitions out of the ground state is classically described by (26) in the spectator or by (30) in the IOS cases. The classical equation (37) can be immediately derived from a simple vector model and the classical weight function appearing in the integrand, which can be shown to be the classical limit of the quantum weights (36) has an obvious geometrical interpretation [6, 78]. The structure of the classical distributions $P_C(J' \rightarrow J|\vartheta)$ has been studied in detail [6, 72]. There is a logarithmic singularity at $J' = J_R - J$ and finite steps at the boundaries of the classically allowed region $J' = J_R + J$ and $J' = J - J_R$. An additional logarithmic singularity may appear at $J' = J$ if the $P_C(J \rightarrow 0|\vartheta)$ probability is finite at $J = 0$. This is the case for IOS cross sections, but not for the spectator model, so that there is no such singularity in the latter case.

In figure 10 the basic features of the factorization formula (35) is illustrated for the spectator model using a fixed value of $\Delta = 20$. The probabilities $P(j'' \rightarrow 0 | \vartheta)$ calculated by the spectator model are used as input, and the transition probabilities are shown as a function of the initial and final quantum numbers $j$ and $j'$. The $0 \rightarrow j'$ transition probabilities accentuated by a thick line show the typical rotational rainbow structure discussed in the preceding section. The quantum-mechanical structure shown in figure 10 possesses a ridge of maxima along the classical singularities at $J' = J_R - J$ and an exponential fall off at the forbidden sides of the classical steps. In the allowed region the distribution shows typical rainbow oscillations.

For initially excited diatomics in the IOS the factorization formula (35) produces a similar distribution as the one shown in figure 10. The main difference is the existence of an additional maximum ridge at $J' = J$ in the quantum-mechanical rainbow patterns. Because the classical IOS probabilities in (30) are not proportional to the final $J$ the classical distribution shows a line of singularities there [72].

2.3. $m$-changing collisions

Though in this review we focus on rotational rainbow effects in state-to-state $j \rightarrow j'$ cross sections it will be profitable to include a short discussion about the much more detailed $j, m \rightarrow j', m'$ transitions, which have been summed and averaged in the theoretical treatment above. Such $m$-changing transitions in atom–diatomic molecule scattering are becoming more and more feasible for experimental studies and are also of considerable theoretical interest, because they provide the most detailed information and can therefore be used as a test of approximation methods. The interested reader should consult the review article by McCaffery et al [77] for more details. Here we are concerned with strong coupling sudden collisions and we point out right
at the beginning that under these conditions nothing new can be learned from an observation of the detailed transitions between the $m$ sublevels for a given system.

The $m$-changing cross sections depend strongly on the chosen quantization axis, which will be fixed as the scattering axis in the following. The most straightforward analysis of $m$-changing transitions is given by the impulsive spectator model (see section 2.1.2), which leads to [67]

$$\frac{d\sigma}{d\Omega}(jm \leftarrow 00|\theta) = P_jm(\theta) \frac{d\sigma}{d\Omega}(j \leftarrow 0|\theta)$$

(38)

for transitions out of the ground state, where the conditional probability for a final $m = -j, \ldots, +j$ is given by

$$P_{jm}(\theta) = \frac{(j - m)!}{(j + m)!} |P_jm(\cos \alpha)|^2$$

(39)

where $P_jm$ is an associated Legendre polynomial and $\alpha$ is the angle between $\Delta k$ and the scattering axis, which is related to the scattering angle $\vartheta$ by

$$\cos \alpha = \frac{k - k' \cos \vartheta}{\sqrt{k^2 + k'^2 - 2kk' \cos \vartheta}}$$

(40)

which reduces to $\sin \alpha \approx \cos \vartheta/2$ for $k' \approx k$. The factorization (38), (39) is a consequence of the orthogonality of $J$ and $\Delta k$ (the 'kinematic apse'), which leads to the selection rule $\Delta m = 0$ with respect to the kinematic apse, and the statistical distribution of the initial molecular orientation, yielding a uniform distribution of the final $J$-vectors on a circle orthogonal to the kinematic apse (compare figure 11). Projection onto the scattering axis leads to a classical probability distribution

$$P_C(M, J) = \frac{1}{\pi \sqrt{M_{\text{max}}^2 - M^2}}$$

(41)
for the projection $M$ of the classical rotational momentum $J$ (note that $J = j + \frac{1}{2}$ and $M = m$ semiclassically). The maximum classical projection is given by $M_{\text{max}} = J \sin \alpha \approx J \cos \frac{\theta}{2}$. There are no $\Delta m$ transitions for backward scattering and, keeping the final $j$ at a fixed value, the maximum classically allowed final values of $M$ are in the forward scattering zone (compare the discussion in [68]).

These results have been known since 1977 for the spectator model [68] and are discussed again within the framework of the $\text{ios}$ approximation [79]. Here the cross sections for the detailed $\Delta m$ transitions depend very much on the choice of the effective orbital angular momentum, $\tilde{\mathbf{e}}$, and for the suggested choice of averaging between initial and final values, $\tilde{\mathbf{e}} = (\ell + \ell')/2$, good agreement between $\text{ios}$ and spectator results (38), (39) was reported [79]. Furthermore classical trajectory calculations have strongly supported this model [80]. Figure 12 compares spectator and classical statistical (equation (41)) transition probabilities with $\text{ios}$ results for two collision energies. Note, that the classical and quantum spectator probabilities, $P_{j \ell m}$, do not depend on the energy.

The overall structure of the transition probabilities for $m$-changing collisions is very similar to the rotational rainbow pattern for $0 \rightarrow j$ transitions. In fact, one can also talk about $\Delta m$ rainbows, which is additionally supported by the square root singularity appearing at the boundary of the classically allowed region at $M_{\text{max}}$. For a discussion of the manifestation of this $\Delta m$ rainbow in the integral cross sections for $0, 0 \rightarrow j, m$ transitions see [68].

Let us finally proceed to $m$-changing collisions for initially rotationally excited molecules, where we have to understand the detailed differential cross sections for $j, m \rightarrow j', m'$ transitions. First an equivalent of (32) can be derived by choosing the scattering axis as quantization axis, where the form factors satisfy the factorization equation

$$F_{j'm'j'm}(\theta) = \sum_{j''m''} C_{j'm'j'm}^{j''m''} F_{j''m''00}(\theta)$$

(42)

with $\theta$ independent coefficients $C_{j'm'j'm}^{j''m''}$ defined in (33). The cross sections are given by (34). The phases of the amplitudes lead to interference oscillations in the $|F_{j'm'j'm}|^2$, which are quenched, however, because of the summation over $j''$ in (42). Neglecting the interference terms one obtains [81]

$$\frac{d\sigma}{d\Omega} (j'm' \leftarrow jm|\theta) = \sum_{j''m''} g_{j'm'j'm}^{j''m''} \frac{d\sigma}{d\Omega} (j''m'' \leftarrow 00|\theta)$$

(43)
Figure 12. Comparison of the spectator model (×) and Δm transition probabilities for He–Na₂ for θ = 100° and 0 → j = 10 at two collision energies, 0.1 eV (●) and 0.15 eV (○). Also shown are classical statistical results (—) (— —). (Adapted from [79]).

Therefore using (38) and (39) all detailed j m → j′ m′ cross sections can be constructed when the degeneracy-averaged ones, \( d\sigma(j'' \rightarrow 0)/dΩ \), are known. Contrary to the case of the degeneracy-averaged rotational factorization (35), however, the Δm factorization (35) is not valid for the integral cross sections because of the θ-dependent weight factors \( P_{jm}(θ) \). A purely classical version of this factorization formula for m-changing collisions has also been developed and tested by means of classical trajectory computations [82].

2.4. Multiple rainbows

In the previous analysis a very simplified picture of the rotational rainbow structure was presented, due to the topological and dynamical simplifications of the collision systems. Additional rainbows and hence more complex structures in the cross sections appear for instance for asymmetric molecules, systems with strong anisotropy, interaction potentials with potential wells or for a more complex dynamics. In the following these situations will be treated separately, though one should be aware of the fact that all of these features may appear together resulting in a very complicated pattern.

Furthermore it is worthwhile noting that multiple rainbows can be produced by different mechanisms as, for instance, by excited initial states of the molecule (see section 2.2), by a more detailed resolution of the state-to-state cross sections (see section 2.3), or by contributions of additional degrees of freedom (see section 4).
24.1. Asymmetric molecules. The symmetry of the interaction potential $V(R, \pi - \gamma) = V(\gamma)$ is not valid for heteronuclear molecules. This is by far the simplest (and best studied) case leading to multiple rotational rainbows. A particularly simple situation occurs for isotopic substituents, where the interaction possesses a symmetry centre, which is, however, shifted from the molecular centre of mass.

For any asymmetric potential the classical rotational rainbow conditions need not be the same on both sides of the molecule and we have two classical rainbows at $J_{R1}$ and $J_{R2}$, and both of them show the characteristic $J_{Ri}(\vartheta) = \dot{J}_i \sin \vartheta/2$ dependence on the scattering angle $\vartheta$. Without loss of generality we can assume $J_{R1} < J_{R2}$ and we note that for heteronuclear molecules the outer rainbow, $J_{R2}$, typically stems from collisions with the lighter molecular atom, simply because of its longer lever arm. These double rainbow effects can be quite dramatic, as demonstrated in figures 13 and 14 by Ios results for two model systems, namely K–CO collision at 1.24 eV, $\vartheta = 150^\circ$ [5] and Na$^+$–CO at 27 eV, $\vartheta = 38^\circ$ [22] (see also the application to He–CO, He–HF [83] and Ar–HF [84]). The Ios approximation for asymmetric molecules is most easily based on equations (6) and (7), where the integral $\int_0^{\pi/2} d\gamma$ is replaced by $\frac{1}{2} \int_0^\pi d\gamma$. This is used in most applications. It should be noted, however, that it may result in systematic phase deviations of the rotational rainbow oscillations, in particular for odd $\Delta j$ transitions (see the detailed discussion by Khare et al [85], where a more refined version of the Ios approximation involving half-integral Legendre functions can also be found).

The interference pattern decorating the double rainbow structure can be easily explained semiclassically [5] (compare section 2.1.1) by observing that on the bright side of the inner rainbow, for $0 < j < J_{R1} - \frac{1}{2}$, we have a ‘four ray’ interference pattern, two of these four contributing classical trajectories (e.g. solutions of (8)–(9)) from collisions with each side of the molecule. Each of these four trajectories carries a phase $\Phi_i$ given by (12) leading to the complex interferences seen in the figures. In the region between the rainbows two of these trajectories become classically forbidden and the oscillatory behaviour is smoothed, resembling the familiar pattern for the homonuclear case with the exception that there is no obvious distinction between

![Figure 13. Differential cross sections for rotational transitions $0 \rightarrow j$ for K–CO collisions at 1.24 eV. Quantum results (full circles) are compared with semiclassical approximations (crosses). (Adapted from [5].)](image-url)
odd and even transitions. Similar observations can be found in many places in the literature [6, 21, 37, 41, 60, 66, 86, 87]. Here we will confine ourselves to some points of general interest:

(i) The lack of symmetry with respect to reflection at the molecular centre of mass leads to a breakdown of the selection rule \( \Delta j \) even'. The population of odd states \((j = 0 \text{ initially})\) with increasing anisotropy can be nicely studied in a spectator model for heteronuclear isotopic molecules, where the transition probabilities are semiclassically proportional to the simple expression [66]

\[
P(j \leftarrow 0 \mid \vartheta) \sim \left| \frac{1}{d_1} \sin (d_1 \Delta k - j \pi/2) + (-1)^j \frac{1}{d_2} \sin (d_2 \Delta k - j \pi/2) \right|^2
\]  

(45)

where \( d_1 \) and \( d_2 \) are the distances of the atoms from the centre of mass. With increasing mass asymmetry \( \delta = |d_2 - d_1| \) the odd transition probabilities related to the two atoms oscillate and are shifted against each other by half a period [66] because of the \((-1)^j\) factor in (45).

(ii) A similar oscillatory pattern can be found in the ratio of all odd to all even transitions [66, figure 4] which has recently been derived in closed form [6, equation (37)] and can be written in a good approximation as

\[
\frac{\sum_{j=\text{odd}} (d\sigma/d\Omega)(j \leftarrow 0 \mid \vartheta)}{\sum_{j=\text{even}} (d\sigma/d\Omega)(j \leftarrow 0 \mid \vartheta)} = \frac{1 - \sin \delta \Delta k / \delta \Delta k}{1 + \sin \delta \Delta k / \delta \Delta k}.
\]  

(46)

With increasing values of the asymmetry \( \delta \) this ratio rises quadratically from zero, it reaches unity (equal probability for odd and even transitions) for \( \delta \Delta k = \pi/2 \) (note that this can happen at quite a small value of \( \delta \) for higher energies) and decays in an oscillatory manner towards unity in the limit of large asymmetries. It is interesting to observe that \( \delta \Delta k \) is exactly equal to the difference of the double rainbows \( |J_{R2} - J_{R1}| \) in the spectator model, which is much larger than \( \pi/2 \) in the 10s examples shown in figures 13 and 14. The destructive interference for odd transitions is restricted to the region below the inner rainbow which is clear from the discussion above.
The effects of a displacement between the centre of symmetry and the centre of mass have been investigated for classical hard-shell scattering [37, 41, 46, 88] and several useful closed form results have been derived in agreement with the features discussed earlier.

It is particularly interesting to note that the asymmetry effects manifesting in the rotational rainbows are sensitive enough to resolve isotopic substitutions, which has been demonstrated for K–C¹⁶O and K–C¹⁸O at 1.24 eV both experimentally and theoretically [37, 60].

The interference effect leading to odd–even oscillations in the final j population for asymmetric target molecules has been experimentally resolved and theoretically reproduced for Ar colliding with NO by Andresen et al [89].

2.4.2. Potential topology. The rotational rainbows described in section 2.1 are characteristic for topologically simple potentials (purely repulsive or attractive, strictly convex hard shell potentials or isoenergetic potential contours, etc). A structural change in the potential leads to a change in the rotational rainbow pattern and the rainbow catastrophes of simple fold type discussed earlier change into higher rainbow catastrophes [2].

This is obvious for anisotropic potentials possessing a potential well. In this case two rainbow features have to be expected: first, a rotational rainbow originating from the anisotropy and, second, an ordinary rainbow originating from the potential well, which is familiar from elastic potential scattering. Numerical experiments with different potential forms accompanied by theoretical analysis have shown that additional cusp-type rainbow singularities appear in the differential state-to-state cross sections. These rainbow features are not independent but must be considered as a manifestation of a combined higher catastrophe, a hyperbolic umbilic. For details see the series of articles [2, 61, 90, 91].

Similar additional rainbows have been discussed for scattering from hard shells, \( R(\gamma) \), differing structurally from the simple convex ellipsoid type, showing, e.g. points of inflection. The relationship between the shape of the hard shell and the (multiple) rotational rainbows has been studied recently for classical scattering in two dimensions [92].

2.4.3. Dynamical effects. Dynamical effects can also change the rotational rainbow structure qualitatively leading to the appearance of multiple rotational rainbows. Basically we can distinguish between two dynamical effects:

First, the collision dynamics is treated in an approximate manner (sudden, IOS, hard shell or spectator model) which reduces the full dynamics considerably, leading to a qualitative change of the cross sections by generating artificial degeneracies. In a full treatment of the dynamics these degeneracies are removed and the rainbow singularities in the reduced dynamics are structurally changed. It has been shown [40] that the classical IOS rainbow square root singularities are changed into a finite step at the maximum accessible value of \( \Delta J \) and a logarithmic singularity at a lower value of the rotational momentum transfer. A second logarithmic singularity appears at low values of \( \Delta j \). These modifications of the dynamically simplified rainbow structures have been confirmed by numerical studies (see, for instance, the classical trajectory results shown in figures 5 and 6).

A second dynamical origin of multiple rainbow structures lies in the occurrence of multiple collisions. In the earlier simplified treatment such multiple impacts have been
neglected. They are, however, important if (i) the potential shape allows a second collision with the target (see the shape effects mentioned above); or (ii) the collision time is comparable with the molecular rotational period, which is, in particular, important when the energy transfer is not negligible and the escaping projectile is slow. The rotor will typically absorb a large rotational momentum in the first impact and in a subsequent second collision some of this momentum is transferred back to the projectile. As a result the differential state-to-state cross sections show a double rainbow structure, where the first impact produces a rotational rainbow at large values of $j$, accompanied by a second one at smaller $j$. For a discussion of multiple collision rainbows see [43, 93–95].

2.5. Inversion techniques

It is widely known that rotationally inelastic cross sections, in particular angular differential and state resolved ones, provide information about the anisotropic intermolecular interaction $V(R, \gamma)$. The inversion techniques try to extract this information from a given set of data. It should be obvious from the discussion of the rotational rainbow features above that in extreme cases, as for instance in electron–Na collisions at collision energies of about $10^2$ eV, only little information can be extracted from the rotational probability distributions at fixed scattering angle. The only molecular parameter which enters the expressions derived from the spectator model is in fact the equilibrium distance, which is known. The situation is different for the atom–molecule collisions under $1s$ conditions. Here the anisotropy is a property of the whole potential surface, which cannot be unambiguously measured in terms of a single variable. Various methods are known for extracting an anisotropic potential from the measured cross sections.

(i) The hard shell inversion [44, 47, 96, 97] is based on the hard-shell model for rotational excitation (compare the introduction of this section). A variety of numerical methods has been suggested, which differ in details. Typically it is assumed first that the observed rotationally inelastic cross sections are due to a rigid shell scattering described by a shell contour of a more or less prescribed form, e.g. $R_x(\gamma) = R_0 (1 + \delta P_2 (\cos \gamma))$ with anisotropy $A = R_0 \delta = 2(R(\theta) - R(\pi/2))/3$, the parameters are determined directly from a few observed quantities, as for instance the rotational rainbow $J_R(\theta) = 3kA \sin \theta/2$, where a measurement of a single rotational rainbow maximum allows a determination of the rainbow position by means of the 44% rule (see section 2.1.1) and hence the anisotropy parameter $\delta$ can be determined. Some drawbacks of this method are that measurements at different scattering angles $\theta$ and different energies may produce different values of $\delta$. The $\theta$ dependence can be cured by assuming a different functional form for the hard shell and the energy dependence can be interpreted by identifying $R(\gamma)$ with the equipotential contour $V(R, \gamma) = E$. In any case the hard shell inversion can only provide an estimate of the anisotropic potential.

(ii) The $1s$ inversion suggested by Schinke [58] is based on the simplified $1s$ model (see section 2.1.1) and proceeds in four steps. First, the total differential cross section $d\sigma / d\Omega (\theta) = \sum_j d\sigma / d\Omega (j|\theta)$ is used to determine the isotropic part, $V_0(R)$, of the potential by a standard inversion technique like the Firsov inversion, which is straightforward for a monotonic potential. This isotropic potential provides the isotropic phase shifts $\delta_i^J$ as well as the classical functional dependence $\ell = \ell(\theta)$, which is assumed to be unique. Second, the anisotropic part of the phase shift $\delta_r^J = \delta_i^J + \delta_r^J(\gamma)$ is expanded in a suitable basis, e.g. $\delta_r^J(\gamma) = \sum_{\nu} a_{\nu}(\ell) \cos^{2\nu} \gamma$, where
where the expansion coefficients \( a_\nu(\ell) \) are computed from a least-squares fit to the available inelastic data at a fixed scattering angle \( \vartheta \), i.e. at a fixed \( \ell \). In step three one fits the \( \ell \) dependence of the \( a_\nu(\ell) \) to a convenient functional form (a polynomial for small values of \( \ell \) matched to a decaying exponential at large values). As a last step another set of Firsov inversions yields the potential \( V(R, \gamma) \) from the phases \( \delta_\ell(\gamma) \), where the orientation angle \( \gamma \) is treated as a parameter. Test calculations for He–Na\(_2\) at 0.1 eV showed satisfying results. The method is, however, numerically quite involved.

(iii) Another method is the deformed inverse power potential (DIPP) inversion proposed recently [56], which combines the simplicity of the hard shell inversion with an increased flexibility. The method assumes that the potential can be written in the form

\[
V(R, \gamma) = E \left( \frac{R_E(\gamma)}{R} \right)^n
\]

where \( R_E(\gamma) \) is the equipotential contour for energy \( E \), which can be specified as \( R_E(\gamma) = R_E(1 + \delta P_2(\cos \gamma)) \). In the region of large scattering angles the rotational rainbows for potential (47) can be obtained in closed form as

\[
J_R(\vartheta) = D_0(E, n) - D_2(E, n)(\pi - \vartheta)^2/8
\]

with

\[
D_\nu(E, n) = 3kR_E\delta d_\nu(n)
\]

and

\[
d_0(n) = \frac{1}{2} B(1 - 1/n, \frac{1}{2}) \quad d_2(n) = n / B(1/n, \frac{1}{2})
\]

where \( B(x, x) = \Gamma(x)\Gamma(y)/\Gamma(x + y) \) is the beta function. In the limit \( n \to \infty \) the DIPP inversion reduces to the hard-shell method. In [56] the \( d_\nu(n) \) coefficients are tabulated. In practice one determines the position of the classical rainbow singularity \( J_R \) from the observed rainbow maxima by means of (14) or the 44% rule. If this is done for at least two scattering angles the parameters \( D_0(E, n) \) and \( D_2(E, n) \) in (48) can calculated from their ratio, the exponent \( n \) and finally the anisotropy parameter \( R_E\delta \). For more details and applications see [56].

3. Polyatomic molecules

The extension of the IAS of section 2.1.1 to the rotational excitation of polyatomic molecules is numerically very expensive and limited by the computational facilities. We refer the reader to [75, 98–103] and confine ourselves in this section to an extension of the two-centre spectator model for rotational excitation to \( N \)-atomic molecules. For simplicity we furthermore restrict the analysis to symmetric tops, in particular to regular planar and bipyramidal targets. We use symmetric top wavefunctions \( |jkm\rangle \), where \( j \) is the rotational quantum number and the quantum numbers
$k$ and $m$ are the projections onto the body-fixed $z$-axis and a space-fixed $Z$-axis, respectively.

The following results are obtained for the highly symmetric case, where all the $N$ atomic constituents are the same, with the possibility of an additional different atom in the molecular centre of mass, which does not induce rotational excitation. In this case simple closed form results for differential rotational state-to-state cross sections or transition probabilities can be derived. Note that the analysis assumes strictly equivalent atomic constituents, which is not necessarily the case if the atoms are the same species, e.g. $O_3$, where the central $O$ atom is expected to interact differently with the scattered particle than the others.

As a direct extension of (20) the molecular form factor is given by [71, 104, 105]

$$F_{j'k'm',jm} = \langle j'k'm' \mid \sum_{l=1}^{N} e^{i\mathbf{d}_l \Delta k} \mid jkm \rangle$$

where $\mathbf{d}_l$ denotes the position vector of the $l$th scattering centre measured from the molecular centre-of-mass.

In the present article we confine the discussion of planar and bipyramidal molecules to transitions out of the rotational ground state $|000\rangle$. Work in the direction of a derivation of a generalized factorization formula is in progress, which relates the excitation of initially rotating molecules to those out of the ground state, similar to the factorization relation for diatomic molecules (35) [114].

### 3.1. Planar molecules

In the case of rotational excitation of planar molecules forming a regular polygon all distances of the $N$ atoms from the centre of mass are equal ($d = |d_j|$) and all angles between the position vectors are equal to $\frac{2\pi}{N}$. The form factor is given by [71]

$$F_{jkm,000} = \left[ (-1)^{(j-k)/2} \frac{(j - k)!}{(j + k)!} \right]^{1/2} \times \frac{\sqrt{\pi} \sqrt{(2j + 1)} 2^j \delta_{m,0}}{\Gamma((j - k)/2 + 1) \Gamma(-(j + k)/2 + \frac{3}{2})} j_j(\Delta)_{k=|k|}$$

$$NS_N^k \begin{cases} 1 & k \geq 0 \\ (-1)^k & k < 0 \end{cases}$$

with $\Delta = d\Delta k$ as defined in (21), where $j_j(\Delta)$ is the spherical Bessel function. The factor

$$S_N^k = \frac{1}{N} \sum_{\nu=1}^{N} e^{-i2\pi k(\nu-1)/N} = \begin{cases} 1 & k = \ldots, -2N, -N, 0, N, 2N, \ldots \\ 0 & \text{else} \end{cases}$$

is a generalization of (23) and states the selection rule that the absolute values of the quantum number $k$ must be an integer multiple of $N$. In addition the singularities of the $\Gamma$ function at non-positive integers yield $F_{jkm,000} \neq 0$ for even values of $j + k$ only, so that for an even number of scattering centres $j$ must be even.
In most cases the detailed transitions to \( k, m \) substates are not resolved and one is only interested in the final \( j \) distribution. For large values of \( \Delta \) the transition probabilities are approximately given by [71, 104]

\[
^N P(j \leftarrow 0 | \theta) = \frac{1}{N} \sum_{k, m = -j}^{j} |F_{jkm, 000}|^2 = (2j + 1) j_j^2(\Delta) \sum_{l=1}^{N} P_j \left( \cos \left[ \frac{2\pi}{N} (l - 1) \right] \right)
\]

(54)

where the \( P_j(x) \) are Legendre polynomials. For the case of a linear molecule \((N = 2)\) this formula agrees with (25).

If \( N \) is even the sum in (54) vanishes for odd values of \( j \) and in agreement with the selection rule \( j = \text{even} \) for \( N = \text{even} \). In the case of odd \( N \) no selection rule exists. Because the Legendre function equals unity for \( j = 0 \) and decreases to zero with increasing \( j \), for small values of \( j \) the propensity rule \( j \approx 0, N, 2N, 3N, \ldots \), is observable. These propensity rules are less pronounced for increasing values of \( j \).

A detailed discussion for small molecules \((N \leq 4)\) is given in the following. Figure 15 shows the quantum transition probabilities results \( P(j \leftarrow 0 | \theta) \) in comparison with the classical results (26).

The case \( N = 2 \) shows the typical rotational rainbow pattern discussed above. For three scattering centres (trigonal molecules, see table 1) the selection rule \( k = \ldots , -6, -3, 0, 3, 6, \ldots \) exists, but only transitions to state \( j = 1 \) are rigorously forbidden. All other transitions are, in principle, allowed. Even values of \( k \) contribute to even \( j \) and odd values of \( k \) to odd \( j \) with the result

\[
^3 P(j \leftarrow 0 | \theta) = (2j + 1) j_j^2(\Delta) \left[ 1 + (-1)^j 2 P_j \left( \frac{1}{2} \right) \right].
\]

(55)

The rotational rainbow pattern shown in figure 15(b) is similar to the distribution of the diatomic targets but no selection rule for \( j \) exists. However, because the Legendre function \( P_j(0.5) \) is unity for \( j = 0 \) and decays to zero for \( j \rightarrow \infty \), for small values of \( j \) the propensity rule \( j \approx 0, 3, 6, 9, \ldots \) is observed.

### Table 1. Structures of molecules (see, e.g., [113]) treated by the spectator model.

<table>
<thead>
<tr>
<th>( N )</th>
<th>Geometrical structure</th>
<th>Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
<td>( \text{N}_2, \text{N}_2, \text{H}_2, \text{CO}_2, \text{HgCl}_2, \text{CuCl}_2 )</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
<td>( \text{BF}_3, \text{HgCl}_3 )</td>
</tr>
<tr>
<td>4</td>
<td>Quadratic planar</td>
<td>( \text{XeF}_4, \text{IF}_4 )</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
<td>( \text{PCl}_5, \text{SnCl}_5^- )</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral or quadratic bipyramidal</td>
<td>( \text{SF}_6, \text{PF}_6^-, \text{SiF}_6^2^- )</td>
</tr>
<tr>
<td>7</td>
<td>Pentagonal bipyramidal</td>
<td>( \text{IF}_7 )</td>
</tr>
</tbody>
</table>

Finally for quadratic planar molecules \((N = 4, \text{see table 1})\) the selection rule \( k = \ldots , -8, -4, 0, 4, 8, \ldots \) exists and consequently \( j \) must be even. The transition
Fire is. Tie quanium mecnanieai (.j and dassicai probabiiitics ior miaiionai uan-
\[ \]tions 0 of N-centre target molecules. The classical rainbow singularity (26) is
chosen as $\Delta = 27.33$. Top, for a two-centre molecule; middle, for a three-centre
molecule (equilateral triangle); bottom, for a quadratic planar molecule.

Probabilities are given by

\[ ^4 P(j \leftarrow 0 | \theta) = (2j + 1)j^2(\Delta) \left[ 1 + (-1)^j + 2 \cdot P_j(0) \right] \]

\[ = 2(2j + 1)j^2(\Delta) \begin{cases} 1 + (-1)^{j/2}(j - 1)!!/(2j)!! & \text{if } j \text{ is even} \\ 0 & \text{if } j \text{ is odd.} \end{cases} \]  

The overall behaviour of the transition probability shown in figure 15(c) is again
similar to the case of two and three scattering centres. The rainbow oscillations are,
however, more pronounced for quadratic planar molecules as a consequence of the
different population of the $j$s, which are odd or even multiples of 2. For small values
of $j$ we find again a propensity rule $j \approx 0, 4, 8, 12, \ldots$, which is more and more
violated with increasing values of $j$.

It should furthermore be pointed out that the angular dependence of the state-
to-state rotational rainbow cross sections structure appears in the argument of the
Bessel functions $j_j (r\Delta k \sin \theta/2)$, which is not at all influenced by the number of
scattering centres and shows the same pattern as in the case of diatomic molecules
in figures 9 and 15(a).
3.2. Bipyramidal molecules

A further extension of the spectator model for linear and planar molecules to bipyramidal symmetric top molecules can be found in [105], where the scattering centres were also assumed to be equivalent. Bipyramidal targets consist of \( N \) atoms forming a regular polygon (the ground plane) with two additional top atoms attached to both sides at the same distance from the ground plane (note that the molecule possesses \( N + 2 \) scattering centres). Examples of bipyramidal molecules are given in table 1.

Using the general form factor for symmetric tops given in (51) and the results of sections 2.1.2 and 3.1 the spectator rotational transition probabilities are found to be

\[
N+2P(j \to 0|\vartheta) = \frac{2j+1}{N+2}\left\{2[1+(-1)^j]j^2(\Delta_\vartheta) + 4Nj_\vartheta(\Delta_\vartheta)j_j(\Delta_\rho)P_j(0)
\right.
\]

\[
\left. + Nj^2_\rho(\Delta_\rho)\sum_{l=1}^{N} P_j(\cos[(l-1)2\pi/N])\right\}
\]  

(57)

with

\[
\Delta_\vartheta = 2d_t k \sin \vartheta / 2 \quad \text{for} \quad i \equiv t, p
\]  

(58)

where \( d_t \) is the distance of the top atoms and \( d_p \) the distance of the ground plane atoms from the centre of mass. For bipyramidal targets the same selection rule as for planar targets of section 3.1 is valid, i.e. only for even \( N \) does the selection rule \( \Delta j = \text{even} \) exist.

Figure 16 shows the rotational transition probabilities in comparison with the classical distributions [6, 105] for four different numbers, \( N \), of atoms in the ground plane. The parameters are chosen as \( \Delta_\vartheta = 14.5 \) and \( \Delta_\rho = \Delta_\vartheta / 2 \). In all cases the quantum mechanical probabilities show a bimodal distribution, where the two maxima are related to the two classical rainbow singularities. The maximum at lower \( j \) results from an excitation by the ground plane atoms and the other one from the atoms at the tops. The influence of the two top atoms decreases for an increasing number of atoms in the ground plane.

4. Combined rotational–vibrational excitation

In the preceding sections the target molecule has been considered as rigid. Here we address some features of rotationally inelastic cross sections for diatomic molecules with a vibrational degree of freedom described by the intermolecular distance \( r \). The interaction potential generalizes to \( V(\bar{R}, r, \gamma) \) and one has to extend the dynamical approximations discussed above to include the vibration. In particular we consider the two cases of weak and strong coupling.

Let us first discuss the case of weak coupling within the rotational I0S approximation. Here a partial decoupling of the vibrational and rotational dynamics can be achieved. The vibrational degree of freedom is treated exactly by solving numerically
a set of vibrationally coupled radial equations for fixed orientation $\gamma$ and each effective orbital angular momentum $\ell$ which are approximately conserved during the collision. The potential surface enters via the matrix elements $V_{n' n}(R, \gamma) = \langle n'| V(R, r, \gamma) | n \rangle = \int dr \, \phi_{n'}(r) V(R, r, \gamma) \phi_n(r) \). 

Neglecting the $j$ dependence of the vibrational wavefunctions $\phi_n(r)$ and the channel energies, $k_{n j} \approx k_n$, the set of vibrational close-coupling equations decouples from the rotational degree of freedom. In the IOS cross section (7) the term $\exp(2i\delta_\ell) - 1$ is replaced by the vibrational transition matrix elements $T_{n' n}$ and $k_n$ appears in the final expression for the cross section (6) instead of the wavenumber $k$. Note, that within this treatment the rotational factorization formula (compare section 2.2) is also valid for the cross sections of individual vibrational $n \rightarrow n'$ transitions. For more details see [74, 106].

As an example we discuss the numerical application to He–Na$_x$ scattering at a collision energy of 0.09 eV [107]. The collision is predominantly vibrationally elastic (the ratio between $|\Delta n| = 1$ and $|\Delta n| = 0$ cross sections is of the order of $10^{-3}$) and the rotational rainbow pattern within the vibrationally elastic cross sections is only slightly affected by the coupling to the vibrational degree of freedom. The small discrepancies are found to be largest in the backward scattering region, where the small impact parameters favour vibrational transitions [107]. Furthermore rotational rainbow features are also observed for vibrationally inelastic transitions. As an example figure 17 shows differential cross sections for the transitions $n j = 0 0 \rightarrow 1 j$ at fixed scattering angle against the final rotational states $j$. Similar results are given in figure 8 for Li$^+$–N$_2$ for several vibrational transitions $0 0 \rightarrow n j$ at $\vartheta = 150^\circ$. The distributions show a similar rainbow pattern as in the vibrationally elastic or the rigid rotor case and the rotational rainbows appear at roughly the same position as in the vibrationally elastic case. The main differences are the broadening of the rainbow maxima accompanied by a quenching of the rainbow oscillations and the larger values of the cross sections for decreasing scattering angles (see [107] for more details).
As an example for strong vibrational coupling we discuss electron–molecule collisions at a collision energy of about 10^3 eV, which can be analysed by the impulsive spectator model as discussed in section 2.1.2. In this case it is also possible to neglect the vibrational energy transfer to the target, which again simplifies the analysis (for an early application of this model to atom–molecule collisions with an explicit consideration of the rotational and vibrational energy transfer see [65, 67]). In an extension of the spectator model as described in section 2.1.2 to combined rotational–vibrational excitation the inelastic form factor for diatomic molecules is replaced by

\[ F_{n',j',m',n,j,m}(r) = \langle n'|F_{j',m',n,j,m}(r)|n \rangle = \int dr \phi_n(r) F_{j',m',n,j,m}(r) \phi_n(r) \]  

where \( F_{j',m',n,j,m}(r) \) is the the form factor of the rigid rotor (20) for an intermolecular distance \( r = 2d \). Correspondingly the probabilities \( P(n',j',m' \rightarrow n,j,m|\theta) \) are proportional to \( |F_{n',j',m',n,j,m}|^2 \).

The probability for transitions out of the rotational ground state is given by the simple formula

\[ P(n,j' \rightarrow n0|\theta) = (2j'' + 1)[1 + (-1)^j'']|\langle n'|j''n(\Delta kr/2)|n \rangle|^2 \quad j' = \text{even} \]  

and, in the case of \( j \neq 0 \), the factorization formula (35) can be used. Numerical results of this simple model for electron–Na\(_2\) scattering at 150 eV showed good agreement with experiment [28]. The detailed rainbow structure for combined rotational–vibrational transitions will be addressed elsewhere [108].

In the remainder of this section we will discuss the marginal cross sections, where the full details are not required.

First, one can be interested in the vibrational transition probabilities only by averaging over the rotation. Using harmonic vibrational wavefunctions a simple closed
form result for the vibrational transition probabilities at fixed scattering angle can be derived [109, 110]

\[
P(n' \leftarrow 0|\vartheta) = \frac{\sqrt{m\omega/\hbar}}{n'!\Delta k} \gamma(n' + 1/2, [\Delta k/2]^2\hbar/m\omega) \tag{62}
\]

with the atom mass, \(m\), and oscillator frequency, \(\omega\), where \(\gamma(x, y)\) is the incomplete gamma function. Transitions out of vibrationally excited states are described by the equation [109, 111, 115]

\[
P(n' \leftarrow n|\vartheta) = \sum_{n''=|n'-n|}^{n'+n} \tilde{C}_{n''n'n} P(n'' \leftarrow 0|\vartheta) \tag{63}
\]

where the weight coefficients are given by

\[
\tilde{C}_{n''n'n} = (-1)^s \sum_k \binom{n''}{k-n'} \binom{n_>}{k-n''} \binom{n_<}{k-n'}.
\]

Equation (63) shows a complete analogy to the factorization formula (35) for rotational transition probabilities (for more information concerning vibrational factorization and scaling relations for the anharmonic case see [109, 111, 115]).

Second, by summing over all final vibrational states \(n'\) the total rotational transition probabilities are found to be [28, 112]

\[
P(j \leftarrow 0, n|\vartheta) = 2(2j+1) \langle n|j^2(\Delta kr/2)|n \rangle = 2(2j+1) \int dr j^2_j(\Delta kr/2)\phi^2_n(r) \tag{65}
\]

(j even).

For transitions \(P(j' \leftarrow j, n|\vartheta)\) again the rotational factorization formula (35) can be used [112, note that there is a misprint in equation (2), where \(j\) should be replaced by \(0\)]. The transition probabilities \(P(j \leftarrow 0, n|\vartheta)\) show typical rotational rainbow features, which depend on the initial vibrational quantum number \(n\), as illustrated in figure 18 for electron-Na collisions. Harmonic vibrational wavefunctions are used and the classical rigid rotor singularity is chosen as \(J_R = \Delta = 20\). For \(n = 0\) the well known rotational rainbow pattern with a pronounced rainbow maximum is observed. With increasing vibrational quantum number \(n\) the maximum broadens and the rotational rainbow oscillations are quenched, similar to the observations for atom-molecule collisions as shown in figure 17. This can be directly understood by looking at (65), which can be interpreted as an incoherent superposition of rigid rotor contributions weighted by the radial probability density. The broadening of the vibrational wavefunction with increasing \(n\) leads to a broadening of the rainbow maximum and the integration quenches the rainbow oscillations.
5. Concluding remarks

In the present review article we have presented a detailed discussion of various features of rotational rainbow structures in state-to-state cross sections for atom/electron collisions with molecules. It has been emphasized that under sudden conditions amazingly simple models can be constructed allowing a very precise description of experimental results.

Of course, many important features have been only touched upon or not considered at all, such as:

(i) the modifications of rotational rainbow structures for anisotropic interaction potentials with a potential well;
(ii) the manifestation of rotational rainbows in integral cross sections;
(iii) the approximate treatment of the energetic inelasticity \((k_j \neq k_j \neq k)\);
(iv) the possible application of the spectator model or the impulse approximation to atom–molecule scattering at higher collision energies;
(v) the range of validity of the simple dynamical models and their possible improvements;
(vi) the existence of rainbow features in the vibrational distributions, i.e. the vibrational rainbows;
(vii) rotational rainbow structures for initially excited symmetric top molecules;
(viii) the experimental observation of rotational rainbow effects for polyatomic target molecules.

Some of these problems have been solved to some extent but many questions are still open and may be answered in future studies.

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