When diffraction rules the stereodynamics of rotationally inelastic collisions

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Outline

1. Why is stereodynamics important?
2. Two words about the model
3. Ar – NO collisions: model vs. experiment and exact computations
4. Other systems: fingerprints of diffraction
5. Conclusions and outlook
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Why is stereodynamics important?

Usual scattering experiments furnish:
- integral cross sections (overall probability for collision to happen), and
- differential cross sections (probability of scattering into a particular angle)
Why is stereodynamics important?

Integral and differential cross sections miss important features

The only way to obtain complete information about the potential is to measure the angular momentum disposal.
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Integral and differential cross sections miss important features

For instance, how will an NO molecule be rotating after colliding with an Ar atom?
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within the collision plane...
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...or perpendicular to the collision plane?
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Alignment moments

We describe molecular rotation using two alignment moments, $a_0^2$ and $a_2^{2+}$. 
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$$a_{0}^{2} = 1 \quad \rightarrow \quad j' \parallel k$$
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\[ a_0^2 = -\frac{1}{2} \rightarrow j' \perp k \]
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a^2_{2+} = -\frac{\sqrt{3}}{2} \ldots \frac{\sqrt{3}}{2}
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describes the alignment of \( j' \) within the plane perpendicular to \( k \)
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$$a_{2+}^{2} = \frac{\sqrt{3}}{2} \rightarrow j' \perp k; \text{ within the collision plane}$$
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$$a_{2+}^{2} = -\frac{\sqrt{3}}{2} \rightarrow j' \perp k; \text{ perpendicular to the collision plane}$$
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3. Ar – NO collisions: model vs. experiment and exact computations

4. Other systems: fingerprints of diffraction

5. Conclusions and outlook
1. *Sudden approximation*: the collision is much faster than molecular rotation.

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![Diagram showing rotational energy levels](image)

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- $J=0$
- $J=1$
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- The inelastic scattering amplitude can be expressed in terms of the elastic amplitude:

$$f_{i \rightarrow f}(\vartheta) = \langle f | f_{\text{el}}(\vartheta, \xi) | i \rangle$$
2. We consider the molecule to be a perfectly absorptive target with sharp boundaries, and replace the true elastic scattering amplitude $f_{el}(\vartheta)$ by the amplitude for *Fraunhofer diffraction*
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3. The collision energy is high compared with any potential well

$\Rightarrow$ we consider only the “repulsive core” of the potential, neglecting the attractive part
The scattering amplitudes

\[ f_{i \rightarrow f}(\vartheta) = \frac{ikR_0}{4\pi} \sqrt{\frac{2j + 1}{2j' + 1}} J_{|\Delta m|}(kR_0 \vartheta) \sum_{\kappa \neq 0}^{\kappa + \Delta m \text{ even}} \Xi_{\kappa, \Delta m} F_{\kappa, \Delta m} C(j\kappa j'; m\Delta mm') \]

\[ \times C(j\kappa j'; \Omega 0\Omega) \left[ (-1)^\kappa + (-1)^\Delta j \right] \]
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No way to study quantum stereodynamics without the scattering amplitudes

Analytic expressions allow getting insight into the stereodynamics
1 Why is stereodynamics important?

2 Two words about the model

3 Ar – NO collisions: model vs. experiment and exact computations

4 Other systems: fingerprints of diffraction

5 Conclusions and outlook
Results for Ar–NO ($X^2\Pi, j = \frac{1}{2} = \Omega \rightarrow j', \Omega = \frac{1}{2}$) collisions

Experiment and exact theory from Wade et al., Chem. Phys. 301, 261 (2004)

Note the form factor

Mikhail Lemeshko (FHI)

Diffraction rules stereodynamics

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All the stereodynamics comes out of the diffraction by a two-dimensional egg!

![Graphs showing stereodynamics](image-url)
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These correspond to the following distribution of angular momenta:

\[
\begin{array}{c}
\text{j -- distribution} \\
\text{j' -- distribution} \\
\text{k} \\
\end{array}
\]

\[
\begin{array}{c}
\text{k'} \\
\text{collision zone} \\
\end{array}
\]

Distribution of molecular axes:

\[
\begin{array}{c}
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\text{r' -- distribution} \\
\text{k} \\
\end{array}
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Other systems: He – NO ($j = \frac{1}{2} = \Omega \rightarrow j', \Omega = \frac{1}{2}$) at 520 cm$^{-1}$

Different scattering channels for fixed collision energy:
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Different scattering channels for fixed collision energy:

![Diffraction pattern diagram](image-url)
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Different scattering channels for fixed collision energy:

The diffraction patterns have the same fingerprints
Other systems: He – NO \( (j = \frac{1}{2} = \Omega \rightarrow j' = \frac{9}{2}, \Omega = \frac{1}{2}) \)

Let’s try it at different collision energies:

![Graph showing diffraction patterns and form factors for different collision energies.](image)
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Diffraction: oscillations scale with the (size of the molecule)/(de Broglie wavelength)!
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Let’s try it at different collision energies:

The form factors are the same: these are the fingerprints of diffraction

Diffraction: oscillations scale with the (size of the molecule)/(de Broglie wavelength)!

Differences between scaled exact results are due to non-diffractive contributions
Other systems: He – NO, O$_2$, OH, and CaH at 520 cm$^{-1}$

Let’s try different molecules:

Moments are scaled with the (size of the molecule)/(de Broglie wavelength)
Other systems: He – NO, O₂, OH, and CaH at 520 cm⁻¹

Let’s try different molecules:

Moments are scaled with the (size of the molecule)/(de Broglie wavelength)

We see the same fingerprints again!
The fingerprints of diffraction

If you observe such a behaviour of the alignment moments:

![Graph showing the behavior of alignment moments](image)

you know immediately that it comes from diffraction.
The fingerprints of diffraction

Well, probably not always...

\[ a_0^2 \]

\[ a_{2+}^2 \]
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1. We developed an analytic model to study the stereodynamics of rotationally inelastic atom-diatom collisions.
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2. The model results for Ar – NO and He – NO are in an excellent agreement with experiment and exact calculations.
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2. The model results for Ar – NO and He – NO are in an excellent agreement with experiment and exact calculations.

3. We show that all the stereodynamics is due to diffraction of matter waves by a flat hard egg.

Outlook:

- Experiment of Jeff Kay and Dave Chandler on Ne–NO (\(A_2\Sigma\))
- Fingerprints of diffraction in cold collisions?

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Diffraction rules stereodynamics
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Thank you for your attention!