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. P. S. Extensions of the model: refraction of matter waves

6. Conclusions and outlook
Why is stereodynamics important?

Two words about the model

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

Other systems: fingerprints of diffraction

P. S. Extensions of the model: refraction of matter waves

Conclusions and outlook
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.
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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?

Unpolarized $j$
Why is stereodynamics important?

Integral and differential cross sections miss important features

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within the collision plane...
Why is stereodynamics important?

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...or perpendicular to the collision plane?
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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?

Unpolarized $j$

...or perpendicular to the collision plane?

The only way to obtain complete information about the potential is to measure the angular momentum disposal

Polarized, $j' \parallel k$
We describe molecular rotation using two alignment moments, $a^2_0$ and $a^2_{2+}$.
Alignment moments

We describe molecular rotation using two alignment moments, $a_0^2$ and $a_2^2$:

$$a_0^2 = -\frac{1}{2} \ldots 1$$

describes the alignment of $j'$ with respect to the initial relative velocity $k$. 

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$$a_0^2 = 1 \quad \rightarrow \quad j' \parallel k$$
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$$a_0^2 = -\frac{1}{2} \quad \rightarrow \quad j' \perp k$$
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$$a_{2+}^{2} = -\frac{\sqrt{3}}{2} \ldots \frac{\sqrt{3}}{2}$$

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![Diagram showing energy levels](image)

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- $J=1$
- $J=2$
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The Fraunhofer model of molecular collisions


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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

\[ f_{i \rightarrow f}(\vartheta) = \frac{ikR_0}{4\pi} \sqrt{\frac{2j + 1}{2j' + 1}} J_{|\Delta m|}(kR_0 \vartheta) \sum_{\kappa \neq 0, \kappa + \Delta m \text{ even}} \Xi_{\kappa 0} F_{\kappa, \Delta m} C(j \kappa j'; m \Delta mm') \times C(j \kappa j'; \Omega_0 \Omega) \left[ (-1)^{\kappa} + (-1)^{\Delta j} \right] \]
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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 P. S. Extensions of the model: refraction of matter waves

6 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

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Diffraction rules stereodynamics

Doyle’s group seminar 13 / 27
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\[ a_0^2(j') \]

\[ a_{2+}^2(j') \]

\[ j' = 9/2 \]

\[ j' = 17/2 \]

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

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Distribution of molecular axes:
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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:

![Graph showing diffraction patterns with Fraunhofer and exact results for different \(j'\) values.](image)

The diffraction patterns have the same fingerprints.
Other systems: He – NO \((j = \frac{1}{2} = \Omega \rightarrow j', \Omega = \frac{1}{2})\) at 520 cm\(^{-1}\)

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![Graph showing diffraction patterns for different scattering channels.](image)

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![Graph](image_url)
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Diffraction: oscillations scale with the (size of the molecule)/(de Broglie wavelength)!
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Diffraction: oscillations scale with the \((\text{size of the molecule})/(\text{de Broglie wavelength})\)!

Differences between scaled exact results are due to non-diffractive contributions
Other systems: He – NO, O\textsubscript{2}, OH, and CaH at 520 cm\textsuperscript{-1}

Let’s try different molecules:

![Graph showing moments scaled with the size of the molecule/(de Broglie wavelength)]

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:

\[
\begin{align*}
\theta & \quad 0.6 & 0.4 & 0.2 & 0.0 & -0.2 & -0.4 & -0.6 \\
0 & & & & & & & 35 \\
\end{align*}
\]

\[
\begin{align*}
\theta & \quad 0.6 & 0.4 & 0.2 & 0.0 & -0.2 & -0.4 \\
0 & & & & & & & \quad o o o o o o o o \\
\end{align*}
\]

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

Well, probably not always...
Fingerprints of diffraction in cold collisions?

Alignment moments for He – NO \((j = \frac{1}{2} = \Omega \rightarrow j' = \frac{3}{2}, \Omega = \frac{1}{2})\) at 10 cm\(^{-1}\)
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An analytic model of the refractive index of matter waves

Our goal: simple analytic expressions that can be used by experimentalists to estimate the refractive index of matter waves passing through cold atomic or molecular gases

Refractive index of matter waves is proportional to the forward elastic scattering amplitude, averaged over thermal distribution:

$$\eta \sim \langle f_{el}(0) \rangle.$$ 

We combined the Fraunhofer model for the repulsive potential with the WKB treatment for the attractive part, and obtained the following expression:

$$\eta = \frac{2\pi}{\hbar} m_p v_p^2 \left[ i \langle v_r \rangle R_0^2 + \langle v^3/5 r \rangle \left( i^2 \right)^{3/5} \Gamma \left( \frac{3}{5} \right) \left( \frac{3\pi}{16} C_6 \hbar \right)^{2/5} \right]$$

Here $m_p$ and $v_p$ are mass and velocity of atoms in the beam, $\langle v_r \rangle$ and $\langle v^3/5 r \rangle$ are relative velocities averaged over beam- and gas-thermal distribution, $R_0$ is the radius of the repulsive atom-atom potential, $C_6$ gives the long-range interaction.
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Refraction of Li matter waves propagating through Xe gas


Important to include the short-range potential: if we neglect it we get the dashed curves
This approach may be used to treat cold collisions
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We developed an analytic model to study the stereodynamics of rotationally inelastic atom-diatom collisions.

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

We identified the fingerprints of diffraction, which can be used to interpret future experimental results.

Extended version of the model works for refraction, which may be used to treat stereodynamics of cold collisions.

Outlook: Experiment of Jeff Kay and Dave Chandler on Ne–NO(A$_2^2\Sigma$)}
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Diffraction rules stereodynamics.

Doyle’s group seminar 26 / 27.
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Thank you for your attention!