External field control of molecular collisions
Principles of the Quantum Control of Molecular Processes

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PAUL BRUMER
“Experimental and theoretical studies of the Coherent Control of unimolecular processes have seen spectacular growth over the last two decades. By contrast, Coherent Control of collisional processes remains a significant challenge...”

Paul Brumer, DAMOP 2007, Bulletin of the APS
Controlled dynamics

Coherent control (Shapiro, ...)

External field control

Controlled chemistry

Notes:
External electric or magnetic fields may

- Close or open reaction channels
- Break the spherical symmetry of the problem
- Mitigate the role of centrifugal barriers in the reaction
- Induce Feshbach resonances that enhance reactivity
- Suppress or enhance the role of spin-orbit interactions
- Align or orient molecules
- Induce anisotropic interactions
- Confinе translational motion in lower dimensions

and thereby allow for control of molecular collisions
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works at low temperatures!
Temperature scale (Kelvin)
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cold
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- ultra-cold
- cold
Temperature scale (Kelvin)
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- ultra-cold
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- warm
- hot
Temperature scale (Kelvin)

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Laser cooling
Buffer-gas cooling
Stark deceleration of beams
Mechanical slowing
Beam collision
Temperature scale (Kelvin)

- Ultra-cold
  - Evaporative cooling
  - Laser cooling
  - Buffer-gas cooling
  - Stark deceleration of beams
  - Mechanical slowing
  - Beam collision
- Cold
- Warm
- Hot
Evaporative Cooling

More delicate methods: evaporative cooling
Experimental confirmation - 1995
E. A. Cornell, C. E Wieman, W. Ketterle

Ultracold gas of Rb atoms just above the transition temperature $T = 200$ nanoKelvin

Ultracold gas of Rb atoms at $T \sim 0.0000002$ Kelvin
Trap loss...
How do electric fields affect spin relaxation?

- Induce couplings between the rotational levels ($\Delta N = 1$)
- Increase the energy gap between the rotational levels

Controlling Electronic Spin Relaxation of Cold Molecules with Electric Fields

T. V. Tscherebul and R. V. Krems

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(Received 3 June 2006; published 22 August 2006)

Spin relaxation is suppressed
Enhancement of spin relaxation

- First-order Stark effect

Enhancement of spin relaxation (a 3D view)
Spin-changing reactions

Na(\(^2S\)) + CaH(\(^2\Sigma\)) \rightarrow NaH + Ca

Notes:
Li + HF $\rightarrow$ LiF + H reaction

Reaction cross section ($\text{Å}^2$)

Collision energy (K)

Calculation by T. Tscherbul
Collisions of molecules in a microwave cavity

Molecular Hamiltonian: \( H_{\text{mol}} = B N^2 \)

Field Hamiltonian: \( H_f = \hbar \omega (a a^\dagger - \bar{n}) \)

Molecule - Field Hamiltonian: \( H_{\text{mol},f} = -\mu \sqrt{\frac{\hbar \omega}{2 \epsilon_0 V}} \cos \theta \left( a + a^\dagger \right) \)

Basis set: \(|NM_N\rangle|n\rangle\)

The matrix elements of the molecule - field Hamiltonian:

\[
\langle n|\langle NM_N|H_{\text{mol},f}|N'M_N'\rangle|n'\rangle \sim \langle NM_N|\cos \theta|N'M_N'\rangle \times \\
\times \left( \delta_{n,n'+1} + \delta_{n,n'-1} \right)
\]

\[
\langle NM_N|\cos \theta|N'M_N'\rangle \sim \delta_{M_N,M'_N} \left( \delta_{N,N'+1} + \delta_{N,N'-1} \right)
\]
Energy levels of a diatomic molecule in a microwave field
Change of a shape resonance in the presence of microwave radiation

$\omega = 1.9 \text{ B}; \mu \varepsilon_0 = 0.5 \text{ B}$

Cross section for elastic scattering ($\text{Å}^2$)

Collision energy ($\text{cm}^{-1}$)
Electric-field-induced resonances in ultracold mixtures of alkali metal atoms
Feshbach resonance
s-wave elastic scattering

Cross section (Å²)

Magnetic field (Gauss)
s-wave elastic scattering

p-wave elastic scattering

Magnetic field (Gauss)

Cross section ($\text{Å}^2$)
s-wave elastic scattering

p-wave elastic scattering

s → p transition at E=30 kV/cm
Cross section ($\text{Å}^2$) vs. Magnetic field (Gauss)

- Red line: No electric field
- Blue dashed line: Zero electric field

Zero electric field
Zero electric field

100 kV/cm

Cross section (Å²)

Magnetic field (Gauss)
Collisions in confined geometries
Quantum Gases in Confined Geometries

Reactions at ultralow temperatures

A + BC → AB + C

Balakrishnan et al., PRL 80, 3224 (1998)

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Wigner’s laws:
elastic cross section ~ constant
reaction cross section ~ 1/velocity

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Reactions at ultralow temperatures

Wigner’s laws:

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rate ~ velocity \times cross section
elastic rate ~ 0
reaction rate ~ constant

Notes:
Threshold laws for collisions in 2D

In 3D, we have Wigner’s threshold laws for elastic scattering:

\[ \text{collision cross section} \sim v^{2l+2l'} \]

In 2D, there is no \( l \). The Hamiltonian is

\[
H = -\frac{1}{2\mu \rho} \frac{d}{d\rho} \rho \frac{d}{d\rho} + \frac{l_z^2}{2\mu \rho^2} + H_{\text{as}} + V(\rho),
\]

The role of \( l \) is played by \( m \), the projection quantum number.

How are the Wigner’s threshold laws modified, if we confine the system in 2D?
Differential scattering cross section (a.u.)

\[
\hat{H} = -\frac{1}{2\mu} \left[ \frac{1}{R} \frac{\partial}{\partial R} R \frac{\partial}{\partial R} + \frac{1}{R^2} \frac{\partial^2}{\partial^2 \varphi} \right] + \hat{V}(R) + \hat{V}_E(R) + \hat{V}_B + \hat{V}_{hf}
\]

\[
\hat{H} \psi = E \psi \quad \psi = \frac{\phi}{R^{\frac{1}{2}}}
\]

\[
\frac{1}{R} \frac{\partial}{\partial R} R \frac{\partial}{\partial R} \psi = \frac{1}{R} \frac{\partial}{\partial R} R \frac{\partial}{\partial R} \left( \frac{\phi}{R^{\frac{1}{2}}} \right) = R^{-\frac{1}{2}} \frac{\partial^2 \phi}{\partial^2 R} + \frac{1}{4} R^{-\frac{5}{2}} \phi
\]

\[
\psi = \frac{1}{R^{\frac{1}{2}}} \sum_{\alpha} \sum_{m} F_{\alpha m}(R) e^{im\varphi} |\alpha\rangle
\]
Let’s look at low-energy scattering:

In 3D, the Schrödinger’s equation is

\[
-\frac{1}{2\mu R^2} \frac{d}{dR} R^2 \frac{d}{dR} + \frac{l(l + 1)}{2\mu R^2} - 2\mu V(R) \psi(k, R) = -k^2 \psi(k, R)
\]

Consider first the solution to this equation with \( V = 0 \) and \( k = 0 \):

\[
-\frac{1}{2\mu R^2} \frac{d}{dR} R^2 \frac{d}{dR} \psi(k, R) = 0
\]

Let’s look for the solution in the form \( \psi(R, k = 0) = \text{const} R^s \)

The derivative:

\[
\frac{1}{2\mu R^2} \frac{d}{dR} R^2 \frac{d}{dR} R^s = s(s + 1) R^s
\]

Hence, \( s(s + 1) = l(l + 1) \) or \( s = l \) and \( s = -(l + 1) \).
A general solution at $k = 0$ is therefore

$$\psi(k = 0, R) = A_1 R^l + A_2 R^{-(l+1)}$$

Now, for $k \neq 0$, we have a Bessel equation and the general solution

$$\psi(k, R) = A j_l(kR) + B \eta_l(kR)$$

which can be re-written at small $k$ as

$$\psi(k, R) = (kR)^l + \tan \delta_l(kR)^{-(l+1)}$$

For smooth and continuous matching to $k = 0$, we must require

$$\tan \delta_l \sim k^{2l+1}$$

which gives after some manipulation:

elastic scattering cross section $\sim k^{4l}$
Repeating this derivation for 2D, we get

\[
\text{cross section} \sim \frac{1}{k \ln^2 k}, \quad \text{when } m = 0
\]

Using the formalism of Wigner, it is also possible to get the off-diagonal cross sections:

\[
\text{cross section for } m = 0 \rightarrow m' \text{ transitions } \sim k^{2|m| - 1} \frac{1}{\ln^2 k}
\]

and

\[
\text{cross section for } m > 0 \rightarrow m' > 0 \text{ transitions } \sim k^{2|m| + 2|m'| - 1}
\]
Threshold collision laws

<table>
<thead>
<tr>
<th></th>
<th>3D</th>
<th>2D</th>
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</thead>
<tbody>
<tr>
<td><strong>Elastic collisions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>s-wave</td>
<td>$\sigma = \text{const}$</td>
<td>$\sigma \propto \frac{1}{v \ln^2 v}$</td>
</tr>
<tr>
<td>s-wave to non-s-wave</td>
<td>$\sigma \propto v^{2l'}$</td>
<td>$\sigma \propto v^2</td>
</tr>
<tr>
<td>non-s-wave to non-s-wave</td>
<td>$\sigma \propto v^{2l+2l'}$</td>
<td>$\sigma \propto v^2</td>
</tr>
<tr>
<td><strong>Inelastic collisions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>s-wave relaxation</td>
<td>$\sigma \propto 1/v$</td>
<td>$\sigma \propto \frac{1}{v \ln^2 v}$</td>
</tr>
<tr>
<td>non-s-wave relaxation</td>
<td>$\sigma \propto v^{2l-1}$</td>
<td>$\sigma \propto v^2</td>
</tr>
</tbody>
</table>

Why is this interesting?
Suppressed collisional spin relaxation

Enhanced collisional spin relaxation
Challenges for Theory of Cold Molecules

• Quantitative predictions of interaction properties at ultracold Ts
  → difficult but not impossible
  → must involve analysis of experiments
  → must involve rigorous scattering calculations

• Scattering theory for molecular collisions at cold (∼ 1 K) Ts
  → must include external fields
  → uncoupled representation = huge basis sets
  → extended propagation grids

• Scattering theory for reactions of highly excited molecules
  → reactions involving alkali metal atoms and diatoms
  → must include external fields and non-adiabatic couplings
  → similar in difficulty to collision induced dissociation
References

R. V. Krems, PRL 93, 013201 (2004).

Reviews