Towards Controlled Chemistry

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Outline

- Introduction
  - Definition of “cold” and “ultracold”..
  - What’s interesting about cold molecules?
  - Methods to produce cold molecules

- External field control of molecular collisions
  - How electric fields might help cool molecules
  - Collisions in superimposed electric and magnetic fields
  - Collisions of molecules in a microwave cavity

- Ultracold collisions of molecules in two dimensions
  - Reactive collisions in 2D might be supressed
  - Effects of field orientation on collisions

- Outlook: Collision physics and ultra-cold molecules
Cold and ultracold molecules

Cold
Few (\( \sim 5 - 10 \)) partial wave scattering
\( T \sim 0.1 - 1 \text{ K} \)

Ultracold
Single partial wave scattering
\( T \sim 0.000001 \text{ K} \)

Notes:
Why study ultracold molecules?

- New phases of matter
- Molecular BEC
- BEC of polar species
  (Ketterle, Wieman, Cornell, Jin, Pfau, Doyle ...)
- Quantum computation with cold trapped molecules
  (DeMille, Lukin, Doyle ...)
- Test of fundamental symmetries
- Search for time variation of fundamental constants
  (DeMille, Ye, Prentiss, Flambaum ...)

\( \frac{da}{dt} \neq \text{constant?} \)

Chemistry in the quantum regime
Bose-enhanced chemistry
Controlled molecular dynamics
(Balakrishnan, Bohn, Hutson, Dalgarno, Kosloff, Doyle ...)

Notes:
Are chemical reactions possible at such low temperatures?
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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elastic cross section ~ constant
reaction cross section ~ 1/velocity

rate ~ velocity \times \text{ cross section}
elastic rate ~ 0
reaction rate ~ constant

Notes:
Reactions at ultralow temperatures

Quantum Dynamics of Ultracold Na + Na₂ Collisions
Pavel Soldán, Marko T. Cvetič, and Jeremy M. Hutson
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England
Pascal Honvault and Jean-Michel Launay
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(Received 3 May 2002; published 18 September 2002)

Zero temperature reaction rate \( \approx 5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \)

29 June 2001

Chemistry at ultracold temperatures
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Received 22 February 2001; in final form 26 April 2001

\( \text{F} + \text{H}_2 \rightarrow \text{HF} + \text{F} \) reaction: Zero temperature reaction rate \( \approx 10^{-12} \text{ cm}^3 \text{ s}^{-1} \)

Notes:
Chemical reactions do occur at subKelvin temperatures!
Chemical reactions do occur at subKelvin temperatures!
They may be very efficient!

Notes:
How to create ultracold molecules?

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How to create ultracold molecules?

- Photoassociation of ultracold atoms
  (S. Walley, DeMille, Bigelow, Heinzen, Masnou-Seeuws, ...)

- Feshbach resonance sweep
  (Jin, Ketterle, Wieman, Cornell, Heinzen, ...)

- Stark deceleration of molecular beams
  (Meijer, Barker, Peters, Friedrich, ...)

- Skimming
  (Abraham, Shafer-Ray, ...)

- Free expansion
  (Gupta, Friedrich, Hershbach, ...)

- Buffer gas loading
  (Doyle, Peters, ...)

- Optical dipole force slowing
  (DeMille, ...)

- Mechanical slowing
  (Gupta, Hershbach, ...)

- Sympathetic cooling by collisions with ultracold atoms
  (Meijer, ...)

- Billiard-ball-like collisions to stop molecules
  (Chandler, ...)

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
- Confine translational motion in lower dimensions

and thereby allow for control of molecular collisions
Electric field control of electron spin relaxation in molecules
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

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(Received 3 June 2006; published 22 August 2006)

Spin relaxation is suppressed

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 ($^2\Sigma$) → NaH + Ca

Notes:
Trap loss...
Microwave traps for polar molecules

Fig. 2. Energies of dressed states vs. applied microwave electric field strength. State labels are zero-field basis states $|\psi_{Jmn}\rangle$.

Energy levels of a diatomic molecule in a microwave field

![Diagram showing energy levels of a diatomic molecule in a microwave field](image-url)
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: $|N M_N\rangle|n\rangle$

The matrix elements of of the molecule - field Hamiltonian:

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

$$
\langle N M_N|\cos \theta |N' M'_N\rangle \sim \delta_{M_N,M'_N} \left( \delta_{N,N'+1} + \delta_{N,N'-1} \right)
$$
Energy levels of a diatomic molecules in a microwave field

\begin{align*}
a(N=0, \ n=Q) + b(N=1, n=Q-1) + c(N=1, n=Q+1) \\
a(N=0, n=Q-1) + b(N=1, n=Q) + c(N=1, n=Q-2)
\end{align*}
Collisionally induced transitions between field-dressed states

Collision energy: 0.3 cm$^{-1}$

Cross section ($\text{Å}^2$)

$\omega = 1.9 \text{ B}$

$\omega = 1.1 \text{ B}$

$\omega = 0.01 \text{ B}$

$\mu\varepsilon_0$ (in units of rotational constant)
Change of a shape resonance in the presence of microwave radiation

Collision energy (cm$^{-1}$)

Cross section for elastic scattering (Å$^2$)

$\omega = 1.9 \text{ B}; \mu \epsilon_0 = 0.5 \text{ B}$

no field
Threshold laws for collisions in 2D

Sergey Alyabyshev and RK, submitted
Quantum Gases in Confined Geometries

Reactions at ultralow temperatures

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

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

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

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

\[ \psi = \frac{1}{R^{1/2}} \sum_{\alpha} \sum_{m} F_{\alpha m}(R) e^{im\varphi} |\alpha\rangle \]
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 \( k = 0 \):

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

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

## Inelastic collisions

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</tr>
</thead>
<tbody>
<tr>
<td><strong>s-wave relaxation</strong></td>
<td>$\sigma \propto 1/v$</td>
<td>$\sigma \propto \frac{1}{v \ln^2 v}$</td>
<td>$\sigma \propto \frac{1}{v \ln^2 v}$</td>
</tr>
<tr>
<td><strong>non-s-wave relaxation</strong></td>
<td>$\sigma \propto v^{2l-1}$</td>
<td>$\sigma \propto v^2</td>
<td>m</td>
</tr>
</tbody>
</table>
Suppressed collisional spin relaxation

Enhanced collisional spin relaxation
Outline

- External field control of molecular collisions
  
  Electric fields might help cool molecules in a magnetic trap

  Superimposed electric and magnetic fields might dramatically affect the collision dynamics of cold molecules

  Microwave radiation modifies the effective intermolecular interaction

- Ultracold collisions of molecules in two dimensions
  
  Reactive collisions in 2D might be suppressed

  Collision dynamics of molecules in 2D may be sensitive to the relative orientation of an external field and the confinement plane
Outlook: Collision Physics and Ultracold Molecules

Experiments with cold molecules may

- confirm or disprove Wigner’s threshold laws → more insight into long-range interactions
- elucidate rates for chemical reactions at ultracold Ts → ultracold chemistry → lots of applications
- demonstrate the possibility of controlling chemical reactions → controlled chemistry → lots of applications
- make coherent control of bimolecular reactions possible → controlled chemistry
- provide new testground for statistical theories of molecules → new reaction rate theories
References

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

Reviews