Temperature scale (Kelvin)
Temperature scale (Kelvin)

- ultra-cold
- cold
- warm
- hot

Coldest T in the Universe
The first Canadian Center for Research on Ultra-Cold Systems, CRUCS is a research institute that combines the research programs and infrastructure of UBC faculty to study the creation, properties and technological applications of ultracold atoms, molecules, plasmas and condensed matter.

CRUCS is distinguished by a strong synergy of experimental and theoretical research, a wide variety of experimental approaches and a diverse yet unifying set of questions pursued under a single roof of the joint facility.

CRUCS supports graduate students, postdoctoral research fellows and visiting scientists, hosts an AMO seminar series and serves as an international hub for research on ultracold matter in Canada.

With the expertise of the center’s PIs and the financial support from the Canadian Foundation for Innovation, it is our ambition to be the world’s leading center for research on and with ultracold systems.

Coldest T in the universe

Temperature Scale (Kelvin)
Are chemical reactions possible at such low temperatures?
Reactions at ultralow temperatures

A + BC → AB + C

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

Notes:
Reactions at ultralow temperatures

\[ A + BC \rightarrow AB + C \]

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

Notes:
Reactions at ultralow temperatures

\[ \text{A + BC} \rightarrow \text{AB + C} \]

\[ \text{Temperature (K)} \]

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

Notes:
Reactions at ultralow temperatures

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

Notes:
Wigner’s laws:
elastic cross section ~ constant
reaction cross section ~ 1/velocity
rate ~ velocity $\times$ cross section
elastic rate ~ 0
reaction rate ~ constant
Reactions at ultralow temperatures

Quantum Dynamics of Ultracold Na + Na₂ Collisions

Pavel Soldán, Marko T. Cvitaš, and Jeremy M. Hutson
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England
Pascal Honvault and Jean-Michel Launay
UMR 6027 du CNRS, Laboratoire de Physique des Atomes, Lasers, Moléculaires et Surfaces, Université de Rennes, France
(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

N. Balakrishnan *, A. Dalgarino
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Received 22 February 2001; in final form 26 April 2001

\( F + H_2 \rightarrow HF + F \) reaction: Zero temperature reaction rate \( \approx 10^{-12} \text{ cm}^3 \text{ s}^{-1} \)

Notes:
Ultracold chemistry – new regime of chemistry

Possibility to study

• controlled chemical reactions

• quantum effects in chemistry

• detailed mechanisms of chemical reactions

• role of individual ro-vibrational energy levels in determining chemical reactivity

See “Cold Controlled Chemistry”:

R. V. Krems, PCCP 10, 479 (2009)
Ultracold chemistry – new regime of chemistry

Possibility to study

• effects of quantum statistics and many-body physics on chemical reactions

• effects of tunable fine and hyperfine interactions on chemical reactions

• effects of external space symmetry on chemical reactions

See “Cold Controlled Chemistry”:
R. V. Krems, PCCP 10, 479 (2009)
Chemical reactions in magnetic traps
Magnetic trap

Magnetic field

middle of the trap
Spin-changing reactions

\[ \text{Na}(^2S) + \text{CaH}(^2\Sigma) \rightarrow \text{NaH} + \text{Ca} \]
How do electric fields affect spin relaxation?

• Induce couplings between the rotational levels ($N = 1$)
• Increase the energy gap between the rotational levels

Enhancement of spin relaxation

- **First-order Stark effect**

Enhancement of spin relaxation (a 3D view)
Polar molecules in a microwave cavity

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

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

Molecule - Field Interaction: $H_{\text{mol},f} = -\frac{d\epsilon_0}{2\sqrt{N}} (\hat{a} + \hat{a}^\dagger) \cos \chi$

Basis set: $|NM_N\rangle|\bar{N} + n\rangle$

The matrix elements:

$$\langle \bar{N} + n|NM_N|H_{\text{mol},f}|N'M_{N}'\rangle|\bar{N} + n'\rangle \sim \langle NM_N|\cos \chi|N'M_{N}'\rangle \times \left(\delta_{n,n'\!+1} + \delta_{n,n'-1}\right)$$

$$\langle NM_N|\cos \chi|N'M_{N}'\rangle \sim \delta_{M_N,M_{N}'} \left(\delta_{N,N'+1} + \delta_{N,N'-1}\right)$$
Polar molecule in a microwave cavity
Polar molecule in a microwave cavity

\[ \Omega_R = \varepsilon_0 d \] (in units of \( B_e \))

\[ a_0 |N = 0, \tilde{N} \rangle + a_1 |N = 1, \tilde{N} - 1 \rangle \]

\[ a_0 |N = 0, \tilde{N} - 1 \rangle + a_1 |N = 1, \tilde{N} - 2 \rangle \]

- no absolute ground state
Energy (in units of $B_e$)

$M_S = \frac{1}{2}$
$M_S = \frac{1}{2}$
$M_S = -\frac{1}{2}$

Cross section (in units of $\AA^2$)

$\hbar \omega = 1.9 \ B_e; \ \Omega = 1 \ B_e$
$\hbar \omega = 1.9 \ B_e; \ \Omega = 2 \ B_e$

Magnetic field, T
Tuning molecular interactions with Feshbach resonances
Feshbach resonance
S-wave elastic scattering cross section (a.u.)

Magnetic field (Gauss)
Resonances in molecule - molecule collisions

T. V. Tscherbul, Y. V. Suleimanov, V. Aquilanti, and RK,
Microwave-laser-field modification of molecular resonances
Polar molecule in a microwave cavity

\[ \Omega_R = \varepsilon_0 d \text{ (in units of } B_e \text{)} \]

\[ a_0 |N = 0, \bar{N} \rangle + a_1 |N = 1, \bar{N} - 1 \rangle \]

\[ a_0 |N = 0, \bar{N} - 1 \rangle + a_1 |N = 1, \bar{N} - 2 \rangle \]

\[ \text{no absolute ground state} \]
Cross section (in units of Å$^2$)

- $\omega = 0.7 \, \text{B}_e \quad \Omega = 0.20 \, \text{B}_e$
- $\omega = 0.7 \, \text{B}_e \quad \Omega = 0.02 \, \text{B}_e$
- $\omega = 1.9 \, \text{B}_e \quad \Omega = 0.02 \, \text{B}_e$

Calculation by Sergey Alyabyshev

He + NH elastic scattering
Cross section (in units of Å²)

- Black line: $B = 7153.19 \text{ G } \omega = 0.70 B_e$
- Red line: $B = 7153.19 \text{ G } \omega = 0.75 B_e$

$\Omega$ (in units of $B_e$)
Cross section (in units of Å$^2$)

- $B = 7153.19 \text{ G } \Omega = 0.1 B_e$
- $B = 7153.19 \text{ G } \Omega = 0.02 B_e$
- $B = 7153.19 \text{ G } \Omega = 0.01 B_e$

Calculation by Sergey Alyabyshev
Reactions in confined geometries
Quantum Gases in Confined Geometries
Quantum theory of chemical reactions in the presence of electromagnetic fields

T. V. Tscherbul and R. V. Kremes
Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada

(Received 29 April 2008; accepted 12 June 2008; published online 21 July 2008)

We present a theory for rigorous quantum scattering calculations of probabilities for chemical reactions of atoms with diatomic molecules in the presence of an external electric field. The approach is based on the fully uncoupled basis set representation of the total wave function in the space-fixed coordinate frame, the Fock–Delves hyperspherical coordinates, and the adiabatic partitioning of the total Hamiltonian of the reactive system. The adiabatic channel wave functions are expanded in basis sets of hyperangular functions corresponding to different reaction arrangements, and the interactions with external fields are included in each chemical arrangement separately. We apply the theory to examine the effects of electric fields on the chemical reactions of LiF molecules with H atoms and HF molecules with Li atoms at low temperatures and show that electric fields may enhance the probability of chemical reactions and modify reactive scattering resonances by coupling the rotational states of the reactants. Our preliminary results suggest that chemical reactions of polar molecules at temperatures below 1 K can be selectively manipulated with dc electric fields and microwave laser radiation. © 2008 American Institute of Physics. [DOI: 10.1063/1.2954021]

I. INTRODUCTION

An important goal of modern chemical physics is to achieve external control over dynamics of elementary chemical processes.1–7 Manipulating chemical transformations by external dc fields or laser radiation is at the heart of molecular chemistry,1 chemical stereodynamics,3,4 and quantum coherent control of molecular dynamics.6 External electromagnetic fields can be used to orient and align molecules, which restricts the symmetry of the electronic interaction between the reactants in the entrance reaction channel and may result in suppression or enhancement of reaction rates, the phenomenon known as the “steric effect.”8–10 Loesch and coworkers9,11,12 and Friedrich and Herschbach7 demonstrated that rotationally cold polar molecules in the Σ electronic state can be effectively oriented by dc electric fields which was used to study steric effects in molecular spectroscopy,9,13 inelastic scattering,7 and chemical reaction dynamics.14 Loesch and Stienkemeier used a combination of dc electric fields and infrared radiation pumping to explore the effects of molecular alignment in the Li+HF (ν=1, j=1) chemical reaction. Their results indicated that side-on collisions between HF molecules and Li atoms are more likely to result in the reaction than end-on collisions.12 The steric effects observed in experiments with thermal molecular beams are, however, usually weak3 because the kinetic energy of the reactants greatly exceeds the perturbations induced by dc electric fields, even for very polar and heavy molecules such as ICl.12

Friedrich and Herschbach have shown that molecules can also be aligned by laser radiation.14 The laser alignment method can be applied to both polar and nonpolar molecules.15 Larsen et al.16 demonstrated that significant alignment can be achieved with laser fields of 1012 W/cm2. The degree of alignment can be quantified by photoionizing the aligned molecules and examining the angular distributions of the photofragments.15,16 Laser-field alignment has been used to produce high-order harmonics with specific polarization emitted by N2, O2, and CO2 molecules.17 Laser-field alignment can also be used to manipulate the rotational motion of molecules18 or control the branching ratios of the photodissociation products.19 The interaction of molecules with an off-resonant laser light is proportional to the square of the electric-field strength, and substantial alignment can be achieved only with very powerful lasers. Because most lasers have short duty cycles, laser-aligned molecules are normally produced with low densities insufficient for scattering experiments.5,5 Other methods, such as collisional alignment in supersonic expansions,4 produce large quantities of aligned molecules, but the degree of alignment in these experiments20 is often insignificant and difficult to quantify.

The effects of external fields on molecular collisions are significantly more pronounced at low temperatures. The development of experimental techniques for cooling molecules to temperatures near or below 1 K has opened up new possibilities to study controlled chemical reactions.21 Chemical reactions of molecules at cold and ultracold temperatures are accelerated by resonances22,23 tunneling,22,23 threshold phenomena,24 quantum interference,25 and many-body dynamics.25,26 With the development of novel experimental methods for manipulating molecules with electromagnetic fields such as Stark deceleration,27,28 magnetic or electrostatic guiding,29 and the design of a molecular synchrotron,30 it has become possible to study cold chemical reactions in...
Elastic collisions

D. S. Petrov and G. V. Shlyapnikov, PRA 64, 012706 (2001)
3D collision core

Elastic collisions

D. S. Petrov and G. V. Shlyapnikov, PRA 64, 012706 (2001)
Elastic collisions

D. S. Petrov and G. V. Shlyapnikov, PRA 64, 012706 (2001)
$\psi_\alpha(r) = i \sqrt{\pi \eta} \varphi_0(0) \frac{1}{k_\alpha r} \left[ e^{-i k_\alpha r} - S_{\alpha\alpha} e^{i k_\alpha r} \right] \phi_\alpha Y_{00}(\hat{r})$
Elastic collisions

\[ \psi_\alpha(r) = i \sqrt{\pi \eta \varphi_0(0)} \frac{1}{k_\alpha r} \left[ e^{-ik_\alpha r} - S_{\alpha \alpha} e^{ik_\alpha r} \right] \phi_\alpha Y_{00}(\hat{r}) \]

3D collision core

The wave function is proportional to the regular 3D wave function

Asymptotic region

D. S. Petrov and G. V. Shlyapnikov, PRA 64, 012706 (2001)
\[ \psi(\vec{r}') = \left[ \varphi_0(z)e^{i\tilde{q}\cdot \vec{r}} - f_{00}(\varepsilon)\varphi_0(z)\sqrt{\frac{i}{8\pi q\rho}}e^{iq\rho} \right] \phi_\alpha Y_{00}(\hat{r}) \]

3D collision core \[ r_e \] The wave function is proportional to the regular 3D wave function \[ l_0 \] Asymptotic region

\[ \psi_\alpha(r) = i\sqrt{\pi\eta}\varphi_0(0)\frac{1}{k_\alpha r} \left[ e^{-ik_\alpha r} - S_{\alpha\alpha}e^{ik_\alpha r} \right] \phi_\alpha Y_{00}(\hat{r}) \]

Elastic collisions

D. S. Petrov and G. V. Shlyapnikov, PRA 64, 012706 (2001)
Inelastic collisions

\[ r_e \]

Z. Li and RK, PRA 79, 050701 (2009)
Inelastic collisions

Couplings occur in 3D collision core

Z. Li and RK, PRA 79, 050701 (2009)
Inelastic collisions

Couplings occur in 3D collision core

The confined and unconfined channels can be treated separately.

Z. Li and RK, PRA 79, 050701 (2009)
Inelastic collisions

\[ \psi_{sc}^{\alpha' \neq \alpha} = - \sum_{\alpha' \neq \alpha} \sum_{l'} \sum_{m'_l} \nu_{\alpha' l'}^{-\frac{1}{2}} r^{-1} S_{\alpha' l' m'_l \leftarrow \alpha 0 0} \chi \frac{i 2 \pi}{k_{\alpha}} Y_{00}^{*}(\hat{r}_i) e^{i(k_{\alpha} r - l' \pi / 2)} \phi_{\alpha'} Y_{l' m'_l}(\hat{r}) \]

Couplings occur in 3D collision core

The confined and unconfined channels can be treated separately.

Z. Li and RK, PRA 79, 050701 (2009)
Inelastic collisions

\[ \psi_{\text{sc}}^{\alpha' \neq \alpha} = - \sum_{\alpha' \neq \alpha} \sum_{l'} \sum_{m'_l} \nu_{\alpha'}^{-1/2} r^{-1} S_{\alpha' l' m'_l \leftarrow \alpha 00} \chi \frac{i2\pi}{k_{\alpha}} Y_{00}^*(\hat{r}_i) e^{i(k_{\alpha'}r - l'\pi/2)} \phi_{\alpha'} Y_{l' m'_l}(\hat{r}) \]

The confined and unconfined channels can be treated separately.

Couplings occur in 3D collision core

The asymptotic wave function for inelastic collisions:

\[ \psi_{\text{sc}}^{\alpha' \neq \alpha} = \sum_{\alpha' \neq \alpha} \nu_{\alpha'}^{-1/2} f_{\alpha' \leftarrow \alpha} e^{i k_{\alpha'} r} \phi_{\alpha'} \]

Z. Li and RK, PRA 79, 050701 (2009)
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 collision laws

<table>
<thead>
<tr>
<th>Collision</th>
<th>3D</th>
<th>quasi-2D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$-wave elastic</td>
<td>$\sigma = \text{const}$</td>
<td>$\sigma \sim \frac{1}{v \ln^2 v}$</td>
</tr>
<tr>
<td>$s$-wave reaction</td>
<td>$\sigma = 1/v$</td>
<td>$\sigma \sim \frac{1}{v \ln^2 v}$</td>
</tr>
<tr>
<td>$s$-wave to non-$s$-wave</td>
<td>$\sigma \sim v^{2l'}$</td>
<td>$\sigma \sim v^{2</td>
</tr>
<tr>
<td>non-$s$-wave to non-$s$-wave</td>
<td>$\sigma \sim v^{2l+2l'}$</td>
<td>$\sigma \sim v^{2</td>
</tr>
</tbody>
</table>

The work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

6.7. Numerical results

Figure 6. The ratios of inelastic and elastic cross sections for $s\sigma$-wave collisions of $^6$Li and $^{87}$Rb atoms as functions of $l_0$ for $|a| = \mu \omega$.

The initial states are $|12, -12\rangle_{^6Li} \otimes |u, t\rangle_{^{87}Rb}$.

The collision energy is $u - 8 \text{ cm}^{-1}$.

The formalism presented in this Chapter can be applied to describe chemical reactions in an ultracold molecular gas under laser confinement. The index $\alpha'$ in Eq. 6.9 must then include outgoing channels in different chemical arrangements.

To explore the effects of laser confinement on chemical interactions of ultracold molecules, we consider an illustrative example of the reaction $^7$Li $^6$Li $^2$l $^v$ = t, $N = u \rightarrow ^7$Li $^6$Li $^2$l $^r$. The cross sections for elastic scattering and $\omega t$.

6.8. Conclusions

We have developed a formalism for rigorous calculations of cross sections for inelastic and reactive collisions of ultracold atoms and molecules confined in quasi-2D geometry. The approach provides expressions for inelastic and reactive scattering cross sections in terms of the $S$-matrix elements for collisions in 3D and the laser confinement parameters. Our theory makes the analysis of reactive collisions of molecules in confined geometries feasible. Otherwise, one would have to calculate the cross sections by solving numerically the scattering problem in the presence of laser fields, which is at present prohibitively difficult. Using the formalism, we elucidated the general features of inelastic scattering and chemical reactions in ultracold quasi-2D gases of atoms and molecules. We have found that the cross sections for inelastic and chemically reactive collisions are suppressed by the confinement forces. This suppression is generally more significant than the effect of the laser confinement on the probability of elastic scattering. The elastic-to-inelastic collision ratios are therefore enhanced in the presence of a laser confinement. Our results suggest that applying laser confinement in one dimension may stabilize ultracold systems.

$^7\text{Li} + ^6\text{Li}^6\text{Li} \rightarrow ^6\text{Li}^7\text{Li} + ^6\text{Li}$ chemical reaction

![Graph showing the ratios of cross sections for elastic scattering and chemical reactions in quasi-2D and 3D as functions of the confinement strength for $^7\text{Li} v^6\text{Li}^2s v^6\text{Li}=0$, $N=1t$ collisions. The collision energy is $10^{-8}\text{cm}^{-1}$.](image)

Cold molecules and Ultracold Chemistry

- 1998: Magnetic trapping of CaH(2Σ) at \( \sim 0.1 \) K.
- 1998: Photassociation of ultracold atoms
- 2005: Measurements of atom - molecule inelastic scattering at \( \sim 10^{-6} \) K
- 2006: Experimental confirmation of Wigner’s threshold law for inelastic collisions of molecules
- 2008: Precision measurements of collision cross sections using cold beams and trapped molecules
- 2008: Dense ensembles of ultracold KRb and Cs\(_2\) in the ground ro-vibrational state created
- 2008 - 09: Measurements of chemical reactions at ultracold T

To come:

- 2009-10: BEC of molecules in the ro-vibrationally ground state
- 2009: Ultracold controlled chemistry
References

S. V. Alyabychev and R. V. Krems, PRA 80, 033419 (2009).

Reviews


Books

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