REACTIVE AND INELASTIC PROCESSES
IN Na + Na₂ COLLISIONS
AT ULTRALOW ENERGIES

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- Recent experiments on the formation of alkali molecules
  (Cs₂, Rb₂, K₂, ...) at ultracold temperatures
  \( Li₂, Na₂ \)

- Studies of inelastic collisions Rb + Rb₂ at 120 \( \mu K \) in a trap
  (D. Heinzen et al., this conference)

- Future experiments will aim at producing a molecular BEC

- Elastic, inelastic and reactive collisions have different roles in
  the formation and stability of a molecular BEC:
  - elastic collisions are favorable for evaporative cooling
  - inelastic and reactive collisions are a source of heating

- Theoretical studies of alkali atom - molecule collisions are needed

- Here, we present a first study concerning Na
TALK OUTLOOK

- Potential energy surface

- Collision mechanisms

- Methodology for quantum dynamics
  - Inner region: hyperspherical coordinates
  - Outer region: Jacobi coordinates

- Results

  - Elastic scattering
    \[ \text{Na} + \text{Na}_2(v, j = 0) \rightarrow \text{Na} + \text{Na}_2(v, j = 0). \]

  - Quenching processes
    \[ \text{Na} + \text{Na}_2(v, j = 0) \rightarrow \text{Na} + \text{Na}_2(v', j') : \text{inelastic} \]
    \[ \text{Na} + \text{Na}_2(v, j = 0) \rightarrow \text{Na}_2(v', j') + \text{Na} : \text{reactive} \]
    
    \[ \text{with } E_{v, j'} < E_{v, j = 0} \]

- Conclusion and prospects
POTENTIAL ENERGY SURFACE


- Potential can be written as:

$$V(r_1, r_2, r_3) = V_2(r_2) + V_2(r_3) + V_3(r_1, r_2, r_3)$$

where $V_2$ and $V_3$ are the two-body, and three-body terms

- $V_3$ is fitted using a multidimensional interpolation procedure.

- Minimum at equilibrium geometry ($D_{3h}$ symmetry)
  - 1223 K at 8.3 $a_0$ (Full PES)
  - 760 K at 9.8 $a_0$ (2B PES)

- Minimum for collinear geometry
  - 554 K at 9.6 $a_0$ (Full PES)
  - 516 K at 9.8 $a_0$ (2B PES)
POTENTIAL ENERGY SURFACE

Linear geometry

-554 K WELL

Perpendicular geometry

60° geometry

Distances in Å

QUENCHING MECHANISMS

- INELASTIC COLLISION

BEFORE

DURING

AFTER

- REACTIVE COLLISION

BEFORE

- ABSTRACTION

- INSERTION

DURING

AFTER
JACOBI COORDINATES FOR A 3-ATOM SYSTEM

α arrangement

β arrangement

γ arrangement

REACTION REGION
METHODOLOGY

INNER REGION

HYPERSPHERICAL DEMOCRATIC COORDINATES

- **Internal coordinates**

  **Size:** Hyperradius \( \rho = \sqrt{R_x^2 + r_y^2} \)

  **Shape:** Hyperangles \( \theta \) and \( \varphi \)

  \[
  \theta = 2 \arctan \sqrt{\frac{r_y}{R_x}} \quad (0 : \text{linear} ; \pi/2 : \text{symmetric top})
  \]

  \[
  \varphi = \frac{1}{2} \arctan \left( \frac{2R_x r_y}{R_x^2 - r_y^2} \right)
  \]

- **Euler angles** \( \alpha_1 \alpha_2 \alpha_3 \)

  Orientation of BF principal axis frame

  Axis of least inertia : Z axis

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The diagram shows a 3D coordinate system with points A, B, and C, illustrating the orientation and coordinates described in the text.
HAMILTONIAN

\[ H = -\frac{1}{2\mu \rho^2} \frac{\partial}{\partial \rho} \rho^2 \frac{\partial}{\partial \rho} + H + C \]

- 2D Hamiltonian \( H \)

\[ H = \frac{1}{2\mu \rho^2} \left( -\frac{4}{\sin 2\theta} \frac{\partial \sin 2\theta}{\partial \varphi} - \frac{1}{\cos^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{4J_z^2}{\sin^2 \theta} \right) + V \]

Deformation + rotation around \( Z \) + potential energy

- \( C \) coupling terms

\[ C = \frac{1}{2\mu \rho^2} \left( \frac{J_x^2 - J_z^2}{\cos^2 \theta / 2} + \frac{J_y^2}{\cos^2 \theta} - 2iJ_y \frac{\sin \theta}{\cos^2 \theta} \frac{\partial}{\partial \varphi} \right) \]

Remaining rotational terms and Coriolis coupling

- Adiabatic states \( \Phi_{k\Omega} \)

\[ H(\rho_p) \Phi_{k\Omega}(\rho_p; \theta, \varphi) = C_{k\Omega}(\rho_p) \Phi_{k\Omega}(\rho_p; \theta, \varphi) \]

Eigenstates of the fixed \( \rho \), fixed \( \Omega \) hamiltonian \( H \)

Expansion on pseudo–hyperspherical harmonics

Eigenfunctions of \( H \) with \( V = 0 \)

\( (J = 0 \) hyperspherical harmonics when \( \Omega = 0 \)\)
DIABATIC BY SECTOR METHOD

- Partial wave is expanded as

\[ \Psi_{JM} = \frac{1}{\rho^{\delta/2}} \sum_{k\Omega} N_{\Omega}^{JM}(\alpha_1 \alpha_2 \alpha_3) \Phi_{k\Omega}(\rho_p; \theta, \varphi) \ F_{k\Omega}^J(\rho_p; \rho) \]

\( N_{\Omega}^{JM}(\alpha_1 \alpha_2 \alpha_3) \): symmetric top eigenfunctions
\( J, M, \Omega \): total angular momentum, SF and BF projections
\( \rho_p \): center of a sector of size \( \sim 0.1 - 0.2 \sigma_0 \)

- Coupled hyperradial equations

\[ \left( -\frac{1}{2\mu} \frac{d^2}{d\rho^2} + \frac{15}{8\mu \rho^2} - E \right) F_{k\Omega}^J(\rho_p; \rho) + \sum_{k'} \mathcal{H}_{k\Omega}^{k'\Omega} (\rho_p; \rho) \ F_{k'\Omega}^J(\rho_p; \rho) + \sum_{k'\Omega'} \mathcal{C}_{k\Omega,k\Omega'}^J (\rho_p; \rho) \ F_{k'\Omega'}^J(\rho_p; \rho) = 0 \]

\( \mathcal{H} \) is diagonal in \( \Omega \)
\( \mathcal{C} \) couples states with \( \Delta \Omega = 0, \pm1 \pm2 \)

- Logarithmic Derivative Propagator (Johnson–Manolopoulos)

- Basis transformation at sector boundaries
$Na_3$ adiabatic hyperspherical energies

Full potential

Two-body potential
PRESENT METHOD

• ADVANTAGES

PHH form an orthogonal and complete set
No overcompleteness problem
Basis states can describe all dynamical situations
Good for the short range dynamics

• DRAWBACKS

Basis states are expensive to compute: CPU $\sim \rho^6$
Couplings behave as $\sim 1/\rho$ at large distances
Bad for the long range dynamics

SYSTEMS ALREADY STUDIED

($\sim 10 \text{ meV} - 2 \text{ eV energy range}$)

• $H + H_2, F + H_2, \ldots (\sim 1990)$
  Abstraction dynamics

• $N(^2D) + H_2, O(^1D) + H_2, C(^1D) + H_2 (\sim 2000)$
  Insertion dynamics
OUTER REGION

JACOBI COORDINATES

- Arthurs-Dalgarno expansion in each arrangement

\[ \Psi_{JM} = \sum_{\nu jl} Y_{\nu jl}^{JM} (\hat{r}_\lambda \hat{R}_\lambda) \chi_{\lambda lj}(r_\lambda) F_{\lambda lj}(R_\lambda) \]

- Radial functions \( F_{\lambda lj}(R_\lambda) \) are the solution of a set of close-coupling equations

- Regular and irregular solutions obtained by inwards integration

- Matching with inner region wavefunction at a fixed hyperradius \( \rho_m \) permits to extract the \( K, S \) and \( T \) matrices
IMPLEMENTATION ON Na + Na₂ (J = 0) COMPUTER

NEC-SX5 vector supercomputer (IDRIS, Orsay)
(peak performance : 8 GFlops / processor)

BASIS SET CALCULATION

- 400 basis states built from hyperspherical harmonics
  (≈ 2550 – 10100 harmonics, depending on ρ)

- They converge at large ρ to diatom rovibrational states
  (ν = 0, ..., 7 ; j_{max} = 49, 45, 41, 36, 31, 26, 19, 10)

- CPU : 4 h (3 Gflops) ; Memory : 2 Gbytes
SCATTERING CALCULATIONS

- 400 channels

- Boundary between inner and outer region: $50a_0$

- Outer region wavefunction

$$\left(-\frac{1}{2\mu}\frac{d^2}{dR^2} + \frac{l(l+1)}{2\mu R^2} - \frac{C_6}{R^8}\right) F(R) = \frac{k^2}{2\mu} F(R)$$

solved numerically in the range $50 - 10000 \ a_0$

$C_6$: asymptotic coefficient of the isotropic long range dispersion interaction.

- Energy range studied: $1 \ \text{nK} - 20 \ \text{K}$

- Computing time: 180 sec. per energy (3 Gflops)
CROSS SECTIONS

- Elastic and Quenching cross sections are given by

\[ \sigma^{el} = \frac{\pi}{k^2} |T_{ii}|^2 \quad \sigma^Q = \frac{\pi}{k^2} (1 - |1 - T_{ii}|^2) \]

\[ T_{ii} = \alpha + i\beta : \text{diagonal element of transition matrix} \quad T = 1 - S \]

\[ \sigma^{el} = \frac{\pi}{k^2} (\alpha^2 + \beta^2) \quad \sigma^Q = \frac{\pi}{k^2} (2\alpha - \alpha^2 - \beta^2) \]

SCATTERING LENGTH

- When \( l = 0 \), \( \alpha \) and \( \beta \) are proportional to \( k \) when \( k \to 0 \) (Wigner's threshold laws).

One can define a complex scattering length

\[ a = \lim_{k \to 0} \left( \frac{\beta}{2k} - i \frac{\alpha}{2k} \right) \]

(Balakrishnan et al., 1997)

Generalisation of the usual scattering length \( a = -\lim_{k \to 0} \left( \frac{\delta}{k} \right) \)

BEHAVIOUR AT ULTRALOW ENERGIES

\[ \sigma^{el} = 4\pi |a|^2 \sim \text{const} \quad \sigma^Q = -\frac{4\pi}{k} Im(a) \sim E_{\text{coll}}^{-1/2} \]

Rate constants \( K^{el} \sim E_{\text{coll}}^{1/2} \quad K^Q \sim \text{const} \)
COMPLEX SCATTERING LENGTH

Na + Na\(_2\) (v=1, j=0)

- \text{Im}(a) = 119.5
- \text{Re}(T_i)/2k
- \text{Re}(a) = 3.4
- \text{Im}(T_i)/2k

Collision energy (K)
Na + Na₂(v=1, j=0)

- \( k^Q > k^{Q1} \) for \( E < 1 \text{ mK} \)
- \( k^{REAC} > k^{INEL} \)
- \( k^Q \) almost constant for \( E < 10 \mu K \) (Threshold Law)
Na + Na$_2$(v=2, j=0)

Na + Na$_2$(v=3, j=0)
TWO-BODY POTENTIAL

Quenching
Reactive
Inelastic
Elastic

$Na + Na_2(v=1,j=0)$

Rate coefficients (cm$^3$ s$^{-1}$)

Collision energy (K)
PROBABILITIES

\((v = 1, j = 0)\) initial state

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Threshold LAWS

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Quenching

Reactive

Inelastic

Resonances

Collision energy (K)
ROTATIONAL DISTRIBUTIONS

**INELASTIC 1K**

\[ \langle \nu=1, j=0 \rangle \rightarrow \langle \nu=6, j \rangle \]

**REACTIVE 1K**

\[ \langle \nu=1, j=0 \rangle \rightarrow \langle \nu=6, j \rangle \]
VIBRATIONAL DISTRIBUTIONS

\[ (v=3, j=0) \rightarrow v' \]

- **REACTIVE**
- **INELASTIC**

Temperature:
- 1 mK
- 1 K

Final vibrational level: 0, 1, 2, 3
CONCLUSION

- QM dynamics of Na + Na₂ ($j = 0$) at ultracold temperatures for $J = 0$ total orbital angular momentum.

- Elastic cross section has a finite limit at zero energy. Inelastic and reactive rate coefficients have also a finite limit at zero energy.

- Large dependence of cross sections on short range interaction potential. Three-body term has a sizeable influence.

- Large dependence of cross sections on $C_6$ coefficient of long range interaction potential due to formation of zero-energy bound states.

- Quenching > Elastic for $E < 1 \text{ mK}$
- $\kappa \Phi$ constant for $E < 10 \mu \text{K}$
PROSPECTS

- Improvement of code efficiency:
  - Matching between outer and inner region at shorter distances (close-coupling treatment in the outer region)
  - Use of symmetry

- Calculation of $J \neq 0$ partial waves

- Use of a more accurate potential energy surface

- Study of higher vibrational states

- Study of rotational quenching:
  \[ \text{Na} + \text{Na}_2(v = 0, j) \rightarrow \text{Na} + \text{Na}_2(v = 0, j' < j). \]

- Hyperfine interactions (coupling with doublet surface)

- Other systems:
  - Li + \text{Li}_2 (poster by M.T. Cvitas et al., this conference)
  - K + K_2, Rb + Rb_2, ...