Reactive collisions of molecules in external fields

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Is there universality in molecular collisions at finite temperature?
Cs atom in magnetic field:

![Graph A](image1.png)

![Graph B](image2.png)

OH molecule in electric field:

![Graph f](image3.png)

![Graph e](image4.png)
Applications of ultracold molecules:

Cold and Ultracold Molecules: Science, Technology, and Applications,
L. Carr, D. DeMille, R. V. Krems, and J. Ye,

Cold Controlled Chemistry,
R. V. Krems,

Quo vadis, cold molecules?
J. Doyle, B. Friedrich, R. V. Krems, and F. Masnou-Seeuws,
Thermal isolation = confinement of molecules by dc electric, magnetic or laser fields
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Cooling experiments = molecular collisions in external field traps
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Elastic collisions lead to cooling
Reactive collisions lead to trap loss
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Cooling experiments = molecular collisions in external field traps

Elastic collisions lead to cooling
Reactive collisions lead to trap loss

It is critical to understand the effects of external fields on elastic, inelastic and chemically reactive collisions of molecules at cold (~1 K) and ultracold (< 0.001 K) temperatures
Collision theory – basic approach:
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\[ H = H_A + H_B + V \]

\[ H \psi = E \psi \]
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\[ \Psi = \sum_i \sum_j F_{ij} \phi_i^A \phi_j^B \]
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Compute \( \phi^A \) and \( \phi^B \) in the molecule-fixed coordinate frame.
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Couple \textbf{all} angular momenta to re-write

\[ \Psi = \sum_J \sum_i \sum_j C_{J_{i,j}} \psi_{i,j}^J(\phi^A \phi^B) \]
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\[ \Psi = \sum \sum \sum C_{Ji,j} \psi_{ij}^J(\phi^A \phi^B) \]

Since 1960, this is called Arthurs-Dalgarno representation
H-matrix in the Arthurs-Dalgarno representation

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Hamiltonian in the presence of an external field

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The Hamiltonian is depicted in a grid format where the presence of an external field is indicated by the red and blue stars.
Hamiltonian in the presence of an external field

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Couple **all** angular momenta to re-write

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Compute \( \phi^A \) and \( \phi^B \) in the *space-fixed coordinate frame*

Couple *all* angular momenta to re-write

\[ \Psi = \sum_J \sum_i \sum_j C_{ij} \psi_{ij}^J (\phi_i^A \phi_j^B) \]

Since 1960, this is called Arthurs-Dalgarno representation
Fully uncoupled space-fixed representation - example:

Collision of two molecules in the $^{2}\Sigma$ state

$$\Psi = \sum_{i} F_{i} \phi_{i}$$

$$\phi_{i} = |N_{A}M_{N_{A}}\rangle |S_{A}M_{S_{A}}\rangle |N_{B}M_{N_{B}}\rangle |S_{B}M_{S_{B}}\rangle |l m_{l}\rangle$$

where all the momenta are projected onto the field axis.

R. V. Krems and A. Dalgarno, JCP 120, 2296 (2004).
Fully uncoupled space-fixed representation - example:

Collision of two molecules in the $^2\Sigma$ state

$$\Psi = \sum_i F_i \phi_i$$

$$\phi_i = \{|N_A M_{N_A}\rangle|S_A M_{S_A}\rangle|N_B M_{N_B}\rangle|S_B M_{S_B}\rangle|lm_l\rangle\}$$

where all the momenta are projected onto the field axis.

In order to evaluate the matrix of $H$, all terms in the Hamiltonian must be written in the space-fixed coordinate frame.

R. V. Krems and A. Dalgarno, JCP 120, 2296 (2004).
Collisions of molecules

Notes:
Collisions of molecules

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Collisions of molecules

\[ V_{AB}(\mathbf{R}, \mathbf{r}_A, \mathbf{r}_B) = (4\pi)^{3/2} \sum_{\lambda_A \lambda_B \lambda} V_{\lambda_A \lambda_B \lambda}(R, r_A, r_B) \]
\[ \times \sum_{m_{\lambda_A} m_{\lambda_B} m_{\lambda}} \begin{pmatrix} \lambda_A & \lambda_B & \lambda \\ m_{\lambda_A} & m_{\lambda_B} & m_{\lambda} \end{pmatrix} Y_{\lambda_A m_{\lambda_A}}(\hat{r}_A) Y_{\lambda_B m_{\lambda_B}}(\hat{r}_B) Y_{\lambda m_{\lambda}}(\hat{R}) \]

Notes:
Any interaction in the Hamiltonian can be represented as a \textbf{direct product} of spherical tensors defined in the \textit{space-fixed} coordinate frame.
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The collision problem of molecules in external fields is most conveniently formulated in the fully uncoupled space-fixed representation.
Li + HF → LiF + H
Energy diagram of the reaction Li + HF(v=0, j=0)

HF(v=0) to LiF(v=0)

ΔE = 0.080 eV

0.243 eV

0.221 eV

0.221 eV

Electric field
The problem with Jacobi coordinates
Solution: the *hyperspherical* coordinates

Mass Scaled Jacobi Coordinates

\[ \mathbf{S}_\gamma = d_\gamma R_\gamma, \quad \mathbf{s}_\gamma = d_\gamma^{-1} \mathbf{r}_\gamma \]

Delves Hyperspherical Coordinates ← Scaled Jacobi:

\[ \rho^2 = (S_\gamma^2 + s_\gamma^2) \]

\[ \theta_\gamma = \tan^{-1} \left( \frac{s_\gamma}{S_\gamma} \right) \]
How do the new coordinates work?
Basis:

\[ \chi_{\alpha v j}(\theta_\alpha; \rho)|j M_j \rangle|\ell M_\ell \rangle = \chi_{\alpha v j}(\theta_\alpha; \rho) Y_{j M_j}(\hat{r}_\alpha) Y_{\ell M_\ell}(\hat{R}_\alpha) \]

where

\[ \tilde{H}_{\text{mol}} \chi_{\alpha v j}(\theta_\alpha; \rho) = \epsilon_{\alpha v j}(\rho) \chi_{\alpha v j}(\theta_\alpha; \rho) \]

Note that this basis is not orthonormal because the functions of different chemical arrangements overlap. This is taken care of by the transformation:

\[ |\zeta_n \rangle = \frac{1}{\sqrt{\lambda_{n M_j, \ell M_\ell}}} \sum X_{\alpha v j M_j, \ell M_\ell, n} \chi_{\alpha v j}(\theta_\alpha; \rho) |j M_j \rangle|\ell M_\ell \rangle \]
The F+H$_2$ chemical reaction: results for Step I

Energy, eV vs. Hyperradius $\rho$
Quantum theory of chemical reactions in the presence of electromagnetic fields

T. V. Tscherbul\textsuperscript{1)} and R. V. Krems

\textit{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
**Hamiltonian in the presence of an external field**

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Collisions in laser fields
Polar molecules in a microwave cavity

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

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:

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

$$
\langle NM_N | \cos \chi | N'M'_N \rangle \sim \delta_{M_N,M'_N} \left( \delta_{N,N'+1} + \delta_{N,N'-1} \right)
$$
we consider moderate Rabi frequencies different arrangements of raw molecules in the strong-field seeking state the state of the molecule within a photon manifold energy $/B_e$ collision-induced transitions between the microwave field. The total wave function of the collision complex is expanded in the products of field-dressed wave functions (4) and spherical harmonics $|\ell m\ell\rangle$. The probabilities for collision-induced transitions between the microwave field-dressed states (4) are obtained from the solution of the multichannel Schrödinger equation [9, 10].

Figure 1(a) shows the energy levels of CaH in a microwave field as functions of the Rabi frequency at $/B_e = 1.57$. The field-dressed levels are arranged in manifolds separated by multiples of the photon energy $\omega$. We label the states by $|\nu\ell\rangle$, where $\nu$ denotes the state of the molecule within a photon manifold, and $\ell$ labels the photon manifold. We consider collisions of CaH molecules in the strong-field-seeking state $|\nu = \alpha, \ell = 0\rangle$, which corresponds to the ground rotational state $N = 0$ of CaH at zero field. The states of different $\ell$ may interact when $\Omega_R \geq 3B_e$. In this work, we consider moderate Rabi frequencies $0 < \Omega_R < B_e$ suitable for a microwave trapping experiment [12].

Figure 2 shows the cross sections for elastic scattering and inelastic relaxation in CaH–He collisions as functions of $\Omega_R$ at a collision energy of 0.3 cm$^{-1}$. The probabilities for inelastic collisions increase with decreasing the detuning from resonance $\Delta = 2B_e - \omega$. For the off-resonant microwave frequencies of 0.01 and 1.1$B_e$, the inelastic cross sections increase monotonically with increasing $\Omega_R$. At a near-resonant frequency of 1.9$B_e$, the cross sections increase by a factor of $\sim 50$ and show broad oscillations. The difference between the cross sections corresponding to different microwave frequencies becomes smaller with increasing the field strength.

In order to elucidate the propensities for collision-induced transitions in a microwave field, we present in Fig. 3 the state-resolved cross sections for inelastic transitions to various final field-dressed states. As our initial state is the ground state in the $K = 0$ manifold, inelastic relaxation involves transitions between different photon manifolds. Figure 3 shows that the total relaxation probability is determined by two major transitions: $|\alpha, K = 0\rangle \rightarrow |\alpha, K' = -1\rangle$ and $|\alpha, K = 0\rangle \rightarrow |\xi, K = -1\rangle$. The field-dressed states $|\alpha, K = 0\rangle$ and $|\alpha, K' = -1\rangle$ differ exactly by one quantum of microwave field energy. Therefore, the transition $|\alpha, K = 0\rangle \rightarrow |\alpha, K' = -1\rangle$ may be interpreted as a collision process accompanied by absorption of a microwave photon. The molecule-field interaction (2) couples the product states with $\Delta N = \pm 1$ and $\Delta n = \mp 1$, so the strongest couplings occur between the field-dressed states in the adjacent photon manifolds ($\Delta K = \pm 1$). Figure 3 shows that the transitions with the minimal change of $K$ are the most probable, and that the transition probabilities decrease rapidly with increasing...
Polar molecule in a microwave cavity

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

Energy (in units of } B_e) \]

\[ N = 0 \]

\[ N = 1 \]

\[ 2B_e \]
Polar molecule in a microwave cavity

The energy levels of a polar molecule in a microwave cavity as functions of the static interaction potential in the fields-dressed basis. Considerr for exampler the dominant final fields-dressed states can be expanded as

\[ n | \alpha \rangle \]

The probabilities for inelastic relaxation involve transitions between different photon manifolds

\[ n \alpha \rightarrow (n-1) \alpha \]

The molecules-field interaction couples the product states with the minimal change of energy levels of a polar molecule in a microwave cavity as functions of the static interaction potential in the fields-dressed basis.

\[ \Delta \]

\[ \Omega_R \]

\[ 2B_e \]

\[ N=0 \]

\[ N=1 \]

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

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

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

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

- **no mw field**
- $\hbar \omega / B_e = 0.7$; $\Omega / B_e = 0.02$

(a) and (b) show the cross section as a function of magnetic field strength ($B$) for different conditions.

(b) specifically highlights a peak in the cross section, indicating a significant interaction or effect at certain magnetic fields.
Challenges for theory of molecular collisions in external fields

Large basis sets = need decoupling approximations

Lack of accurate intermolecular potentials = need experimental data

Lack of rigorous theories connecting short-range interaction physics and long-range dynamics
Is there universality in molecular collisions at finite temperature?