Collisions of ultracold molecules - beyond the universal regime

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Abstract

Based on the quantum defect theory we develop a framework for reactive collisions applicable for various types of the power-law potentials ($-1/r^n$) and valid from the ultracold up to the high-temperature limit. Our theory is applicable for both universal and non-universal collisons. The former corresponds to the unit reaction probability at short range, while in the latter case the reaction probability is smaller than one. In the non-universal regime we study the influence of shape resonances on the collision rates. In the high-energy limit we present a method that allows to incorporate quantum corrections to the classical reaction rate due to the shape resonances and the quantum tunelling. We present explicit analytical formulas for two physically most relevant power-law potentials: van der Waals ($n=6$) and polarization potential ($n=4$), showing that quantum corrections can be important even at room temperatures for typical atomic species.

Introduction

Radial Schrödinger equation with a complex potential

$$\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}+V_\ell(r)\right)\Psi_{\ell m}(r)=E\Psi_{\ell m}(r),$$

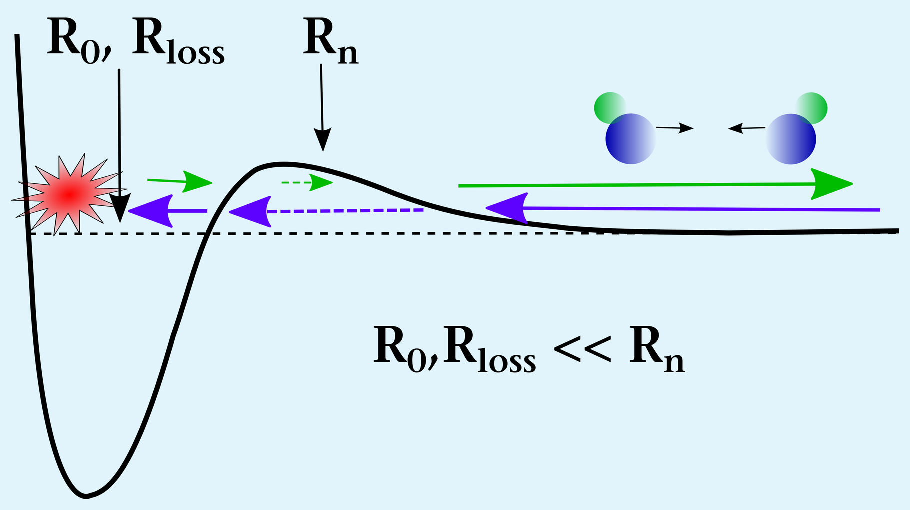
where

$$V_\ell(r)=V(r)+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}-i\frac{\gamma(r)}{2}$$

Assumptions obout interaction potential:
1) power-law potential at long range $V(r)\approx-\frac{C_n}{r^n}$ for $r\geq R_0$,

characteristic energy $E_n=\hbar^2/(2\mu R_n^2)$
characteristic distance $R_n=\left(2\mu C_n/\hbar^2\right)^{1/(n-2)}$

2) losses occur at short range $\gamma(r)\approx 0$ for $r\geq R_{\rm loss}$



We define an energy-dependent complex scattering length

$$\tilde{a}_{\ell m}(E)=\tilde{\alpha}_{\ell m}(E)-i\tilde{\beta}_{\ell m}(E)=\frac{1}{ik}\frac{1-S_{\ell m,\ell m}}{1+S_{\ell m,\ell m}}.$$

defined in terms of the diagonal elements of S matrix. The elastic $\mathcal{K}^{\rm el}$ and the reactive $\mathcal{K}^{\rm re}$ rate constants can be expressed as

$$\mathcal{K}^{\rm el}_{\ell m}(E)=g\frac{\pi\hbar}{\mu k}\left|1-S_{\ell m,\ell m}(E)\right|^2=2g\frac{hk}{\mu}|\tilde{a}_{\ell m}(k)|^2 f_{\ell m}(k)\,,$$

$$\mathcal{K}^{\rm re}_{\ell m}(E)=g\frac{\pi\hbar}{\mu k}\left(1-|S_{\ell m,\ell m}(E)|^2\right)=2g\frac{h}{\mu}\tilde{\beta}_{\ell m}(k)f_{\ell m}(k)\,,$$

where

$$f_{\ell m}(k)=\frac{1}{1+k^2|\tilde{a}_{\ell m}(k)|^2+2k\tilde{\beta}_{\ell m}(k)},$$

At low energies $f_{\ell m}(k)\to 1$ as $k\to 0$, provided $k|\tilde{a}_{\ell m}(k)|\ll 1$ and $k\beta_{\ell m}(k)\ll 1$. In general, $0<f_{\ell m}(k)\leq 1$.

MQDT

A pair of linearly independent solutions that have local WKB-like normalization at short distances

$$\left.\begin{array}{lcl}\hat{f}(r,E)&\cong&k(r)^{-1/2}\sin\beta(r),\\ \hat{g}(r,E)&\cong&k(r)^{-1/2}\cos\beta(r),\end{array}\right\}\quad r\gtrsim R_0.$$

In MQDT one parameterizes the wave function at short range using $\hat{f}$ and $\hat{g}$ functions

$$\Psi(r,E)=A(E)\left[\hat{f}(r,E)-iy\hat{g}(r,E)\right].$$

Here, $A(E)$ is the amplitude. Short range behavior of $\Psi(r)$

$$\Psi(r)\sim\frac{e^{-i\int^r k(x)dx}}{\sqrt{k(r)}}-\left(\frac{1-y}{1+y}\right)\frac{e^{i\int^r k(x)dx}}{\sqrt{k(r)}}.$$

$y=1$ corresponds to unit reaction probability (no outgoing flux) while for $y=0$ there are no losses (incident and reflected fluxes have equal amplitudes). The reaction probability at short range is

$$P^{\rm re}=1-\left[(1-y)/(1+y)\right]^2=4y/(1+y)^2.$$

References

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General Solution

An exact expression for the energy-dependent complex scattering length, which is valid for arbitrary energy and partial wave ℓ

$$\tilde{a}_{\ell m}(E)=-\frac{1}{k}\tan\left[\xi(E,\ell)-\tan^{-1}\left(\frac{yC^{-2}(E,\ell)}{i+y\tan\lambda(E,\ell)}\right)\right].$$

Here, $\xi(E,\ell)$ is the scattering phase shift of the potential $V(r)$, and $C(E)$ and $\tan\lambda(E)$ are the MQDT functions that connect the solutions with short- and long-range normalization. We can express the reaction rate directly in terms of MQDT function

$$\mathcal{K}^{\rm re}_{\ell m}=g\frac{h}{2\mu k}P^{\rm re}\frac{C^{-2}(E,\ell)(1+y)^2}{(1+yC^{-2}(E,\ell))^2+y^2\tan^2\lambda(E,\ell)}.$$

Van der Waals potential (n=6)
Low-energy behavior of MQDT functions

$$C^{-2}(E,\ell=0)\overset{k\to 0}{\longrightarrow}k\bar{a}\left(1+(s-1)^2\right),\quad \tan\lambda(E,\ell=0)\overset{k\to 0}{\longrightarrow}1-s.$$

and $\tan\xi(E,\ell=0)\overset{k\to 0}{\longrightarrow}-ka$, where $s=a/R_n$ is the dimensionless scattering length. In this limit

$$\mathcal{K}^{\rm re}_{00}\overset{E\to 0}{\longrightarrow}2g\frac{h}{\mu}\bar{a}y\frac{1+(1-s)^2}{1+y^2(1-s)^2}.$$

Polarization potential (n=4) Low-energy behavior of MQDT functions

$$C^{-2}(E,\ell=0)\overset{k\to 0}{\longrightarrow}kR^\star\left(1+s^2\right),\quad \tan\lambda(E,\ell=0)\overset{k\to 0}{\longrightarrow}-s,$$

In this limit

$$\mathcal{K}^{\rm re}_{00}\overset{E\to 0}{\longrightarrow}2g\frac{h}{\mu}R^\star y\frac{1+s^2}{1+y^2s^2}.$$

General power-law potential at high energies

$$\mathcal{K}^{\rm re}\overset{E\to\infty}{\longrightarrow}g\frac{h}{2\mu k}P^{\rm re}\ell_{\rm max}(E)\left[1+\ell_{\rm max}(E)\right]$$

where $\ell_{\rm max}(E)$ is the maximal angular momentum at which the top of the barrier is equal to the collision energy E.

$$\mathcal{K}^{\rm re}\overset{E\to\infty}{\longrightarrow}g\frac{h}{2\mu k}P^{\rm re}\frac{n}{2}\left(\frac{E/E_n}{\frac{n}{2}-1}\right)^{(n-2)/n}.$$

This result correspond to the classical limit for the reaction rate.

Shape resonances at large energies

In our approach we first fit the centrifugal barrier to a parabolic potential by equating the first and the second derivative at the maximum of the barrier. Using the exact solution we calculate the S matrix and the reaction probability $P=1-|S|^2$. We average the result over the short-range phase. In this way we incorporate the average effect of the shape resonances on the reaction rates. We find that

$$P_{\ell m}=1-|S_{\ell m,\ell m}|^2=\frac{1}{e^{-2\pi\varepsilon}+\frac{1}{P^{\rm re}}}.$$

where ε is the energy expressed in the harmonic oscillator units

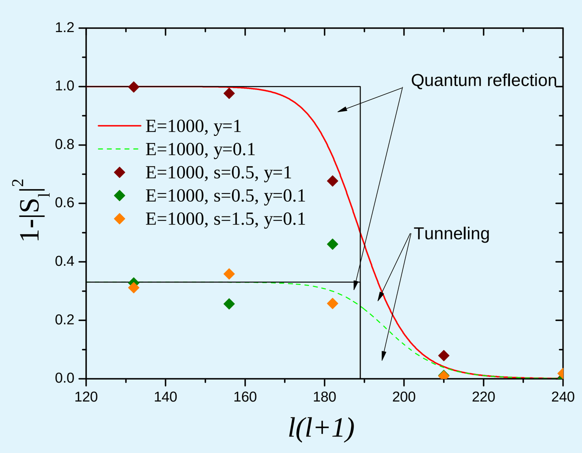
$$\varepsilon(\ell,E)=\frac{\left(\frac{n}{2}\right)^{\frac{2}{n-2}}}{\sqrt{2n-4}}E(l(l+1))^{-\frac{n+2}{2n-4}}-\sqrt{2n-4}\frac{\sqrt{l(l+1)}}{2n}$$

The reaction rate at high energies is given by

$$\mathcal{K}^{\rm re}\overset{E\to\infty}{\longrightarrow}g\frac{h}{2\mu k}\sum_0^{\infty}{}'(2\ell+1)\frac{1}{e^{-2\pi\varepsilon(\ell,E)}+1/P^{\rm re}}$$

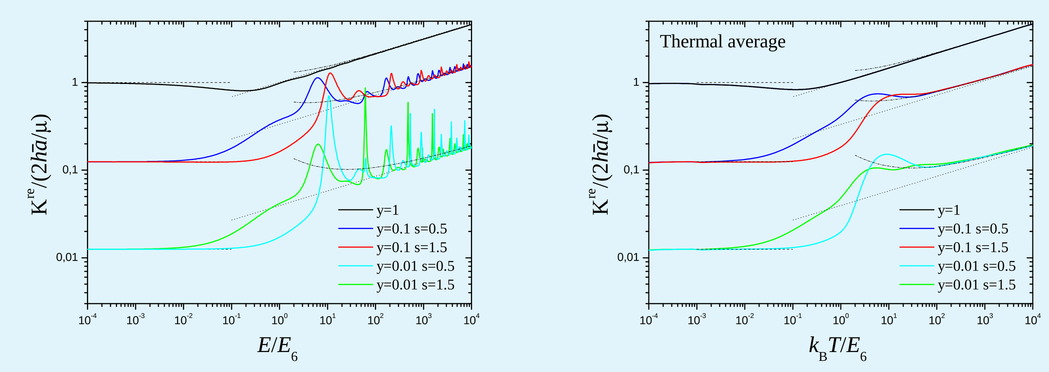
$$\approx\frac{h}{2\mu k}\int_0^\infty\frac{d\left[\ell(\ell+1)\right]}{e^{-2\pi\varepsilon(\ell,E)}+1/P^{\rm re}}$$

where $\sum'$ denotes summation over allowed values of angular momenta. One can replace summation over ℓ by integration using the fact that for indistinguishable particles the summation is done only over even or odd values of ℓ.

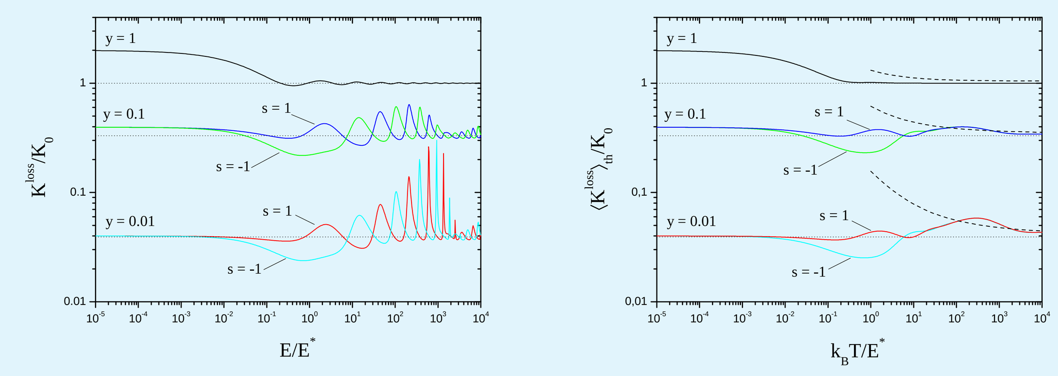


Reaction probability calculated for a parabolic potential fitted to the actual centrifugal barrier of the van der Waals potential versus the angular momentum squared $\ell(\ell+1)$ (red solid dashed and green dashed lines).

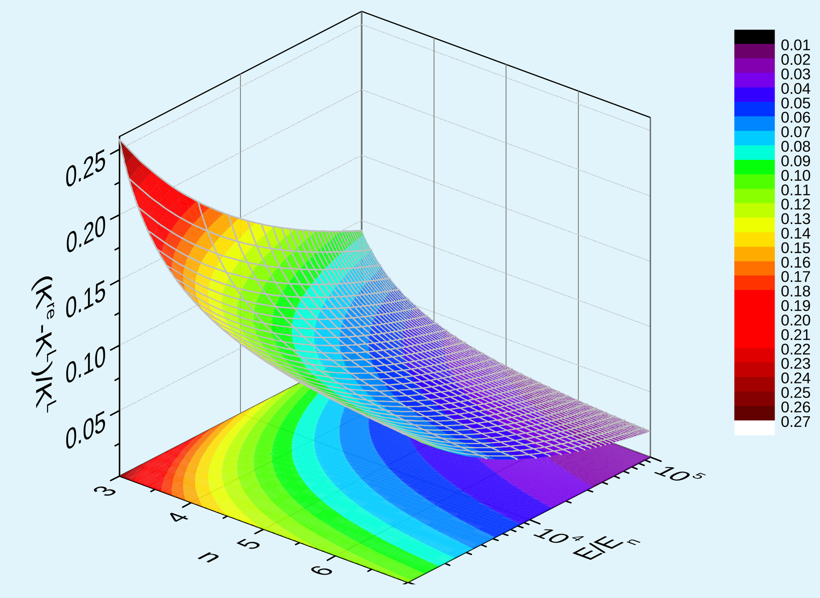
Results



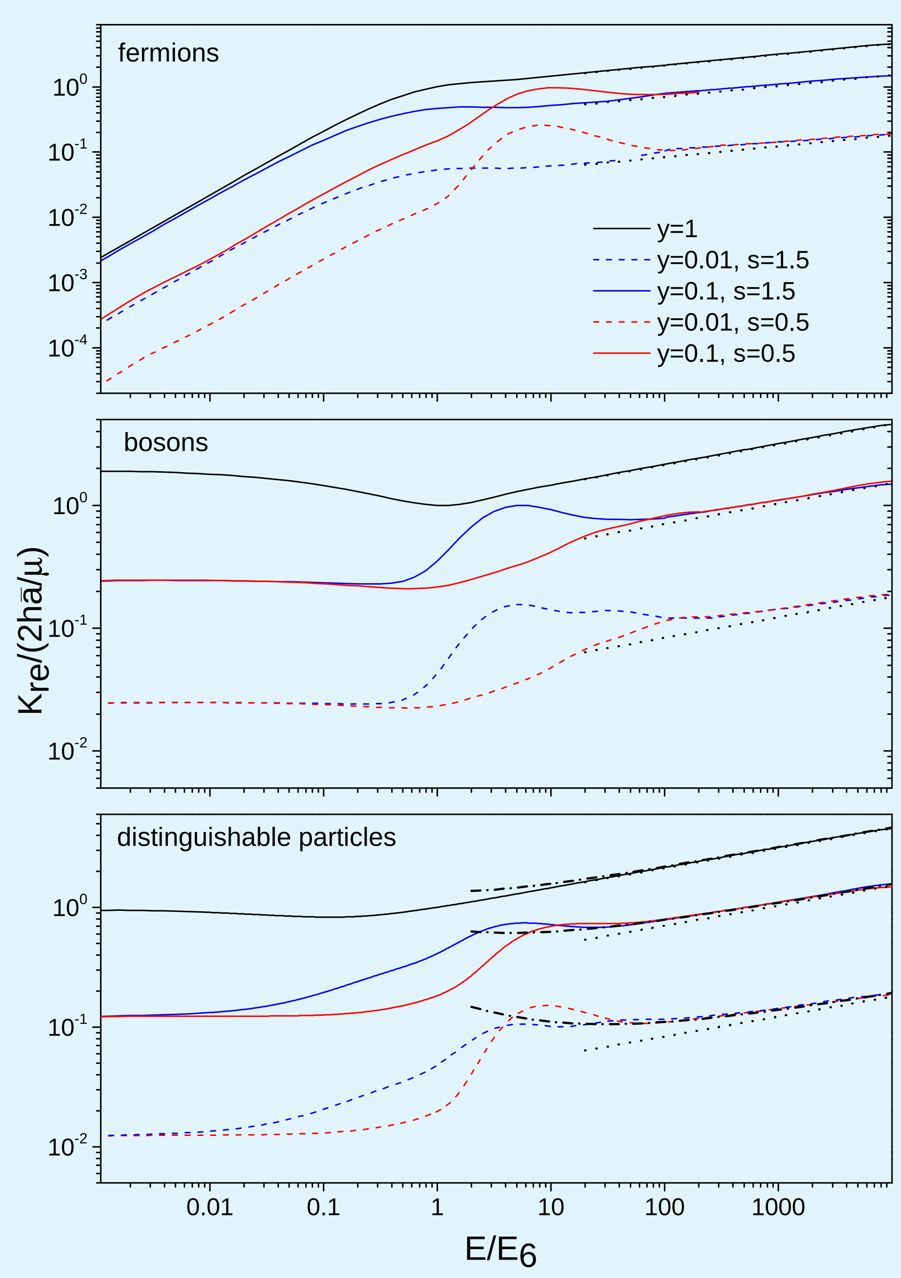
Reactive rates for van der Waals potential with and without thermal averaging. Dashed line - low energy limit, dotted line - classical limit, dot-dashed line - quantum high energy limit.



Reactive rates for polarization potential with and without thermal averaging. Dotted line - classical limit, dashed line - high energy quantum limit.



Quantum corrections for high temperatures.



Thermally averaged reaction rates for van der Waals potential. Dotted line - classical limit, dot-dashed line - high energy quantum limit.

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