Quantum theory of reactive collisions for $1/r^n$ potentials

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Abstract

We develop a general quantum theory for reactive collisions involving power-law potentials valid from the ultracold up to the high-temperature limit. Our quantum defect framework extends the conventional capture models to include the non-universal case when the short-range reaction probability is less than 1. We present explicit analytical formulas as well as numerical studies for the van der Waals and polarization potentials, and relate our work to recent merged beam experiments on Penning ionization for collision energies below 0.1 meV. 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.

Introduction

Radial Schrödinger equation with a complex potential

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

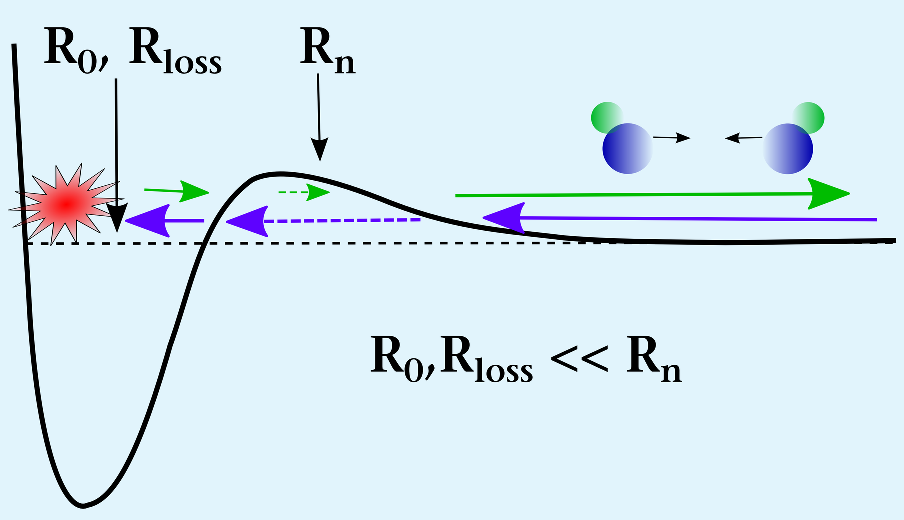
where

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

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

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

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 $\Psi(r)$

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

$y=1$ 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

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

MQDT functions $C(E)$, $\tan\lambda(E)$ connect short- and long range solutions and build in the effect of shape resonances.

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 functions

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

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

$$C^{-2}(E,\ell=0)\xrightarrow{k\to0}k\bar{a}\left(1+(s-1)^2\right),\qquad\tan\lambda(E,\ell=0)\xrightarrow{k\to0}1-s.$$

and $\tan\xi(E,\ell=0)\xrightarrow{k\to0}-ka$, where $s=a/R_n$ is the dimensionless scattering length. In this limit

$$\mathcal{K}^{\rm re}_{00}\xrightarrow{E\to0}2g\frac{h}{\mu}\bar{a}y\frac{1+(1-s)^2}{1+y^2(1-s)^2}.$$

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

$$C^{-2}(E,\ell=0)\xrightarrow{k\to0}kR^\star\left(1+s^2\right),\qquad\tan\lambda(E,\ell=0)\xrightarrow{k\to0}-s,$$

In this limit

$$\mathcal{K}^{\rm re}_{00}\xrightarrow{E\to0}2g\frac{h}{\mu}R^\star y\frac{1+s^2}{1+y^2s^2}.$$

General power-law potential at high energies

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

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

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

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

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

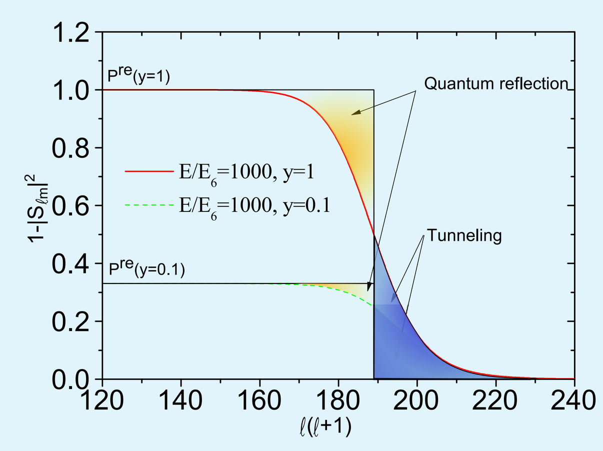
where ε is the energy expressed in the harmonic oscillator units

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

The reaction rate at high energies is given by

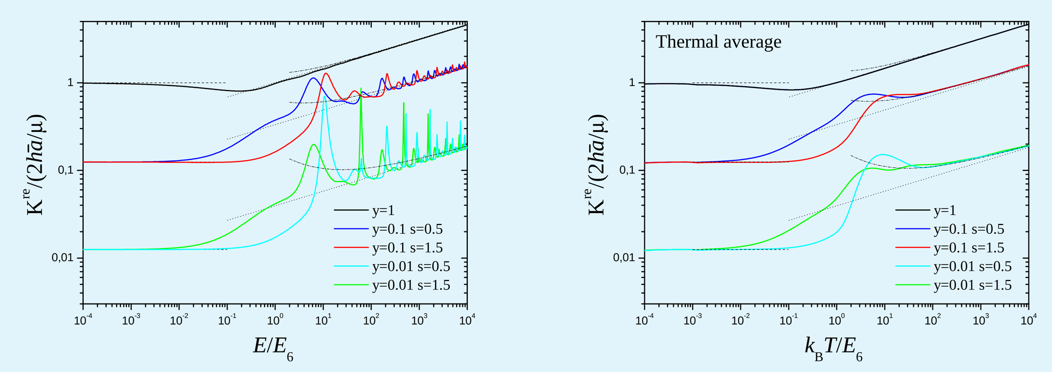
$$\mathcal{K}^{\rm re}\xrightarrow{E\to\infty}g\frac{h}{2\mu k}\sum_0^{\infty}{}'(2\ell+1)\frac{1}{e^{-2\pi\varepsilon(\ell,E)}+1/P^{\rm re}}$$
$$\approx\frac{h}{2\mu k}\int_0^\infty\frac{d\left[\ell(\ell+1)\right]}{e^{-2\pi\varepsilon(\ell,E)}+1/P^{\rm re}}$$

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.

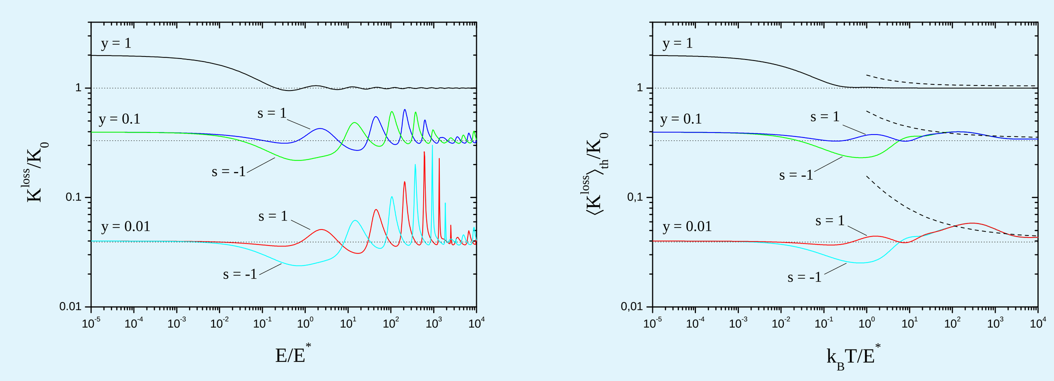


Reaction probability calculated for a parabolic potential fitted to the actual centrifugal barrier of the van der Waals potential versus the angular momentum squared $\ell(\ell+1)$ (red solid dashed and green dashed lines).

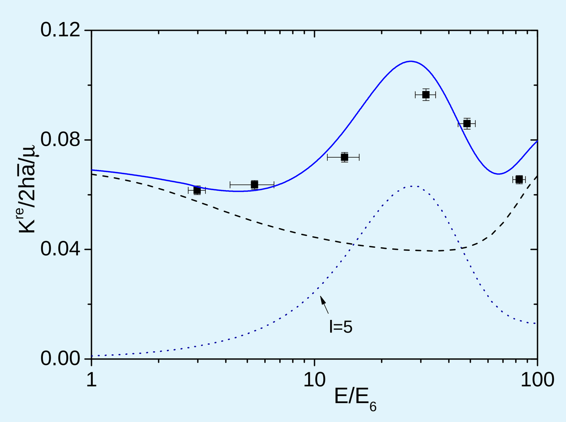
Results



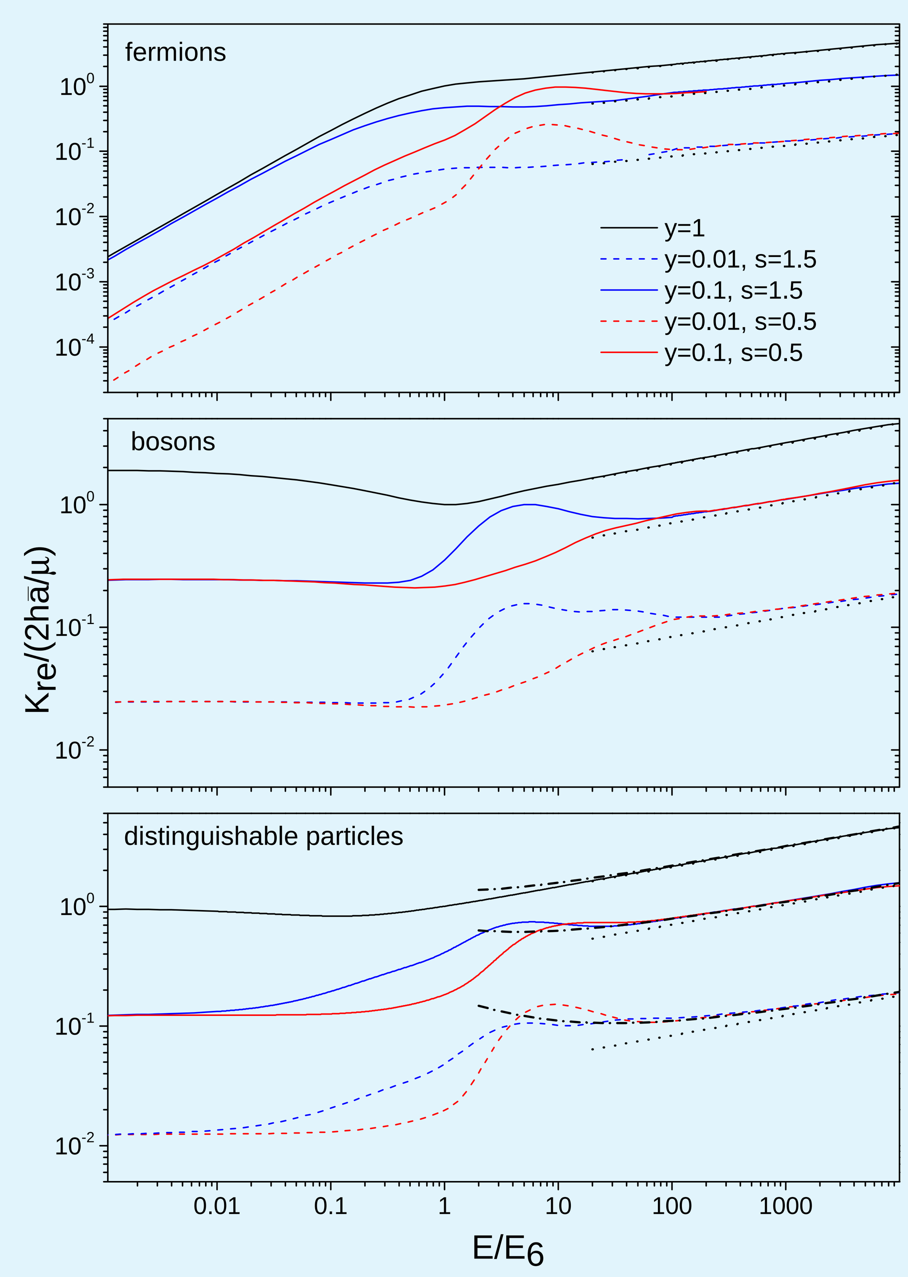
Reactive rates for van der Waals potential with and without thermal averaging. Dashed line - low energy limit, dotted line - classical limit, dot-dashed line - quantum high energy limit.



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



Measured reactive rate constants (black points), QDT fit, contribution from $\ell=5$ and other partial waves for the collision of Ar with He*. Experimental data from Henson et al, Science 338, 234(2012). The fit parameters are $y=0.007$ and $s=3$. For this system $R_6\approx40\,a_0$ and $E_6/k_B\approx14\,mK$. The calculations were averaged over the actual velocity distribution of a merged beam.



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

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