Simulating reaction of Ne* + OCS collision

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1 Improved potential interpolations

Potential is now fitted to the force field instead of interpolation, because of smoothness issues. Gamma potentials now have correct vanishing derivatives for angles 0 and π.

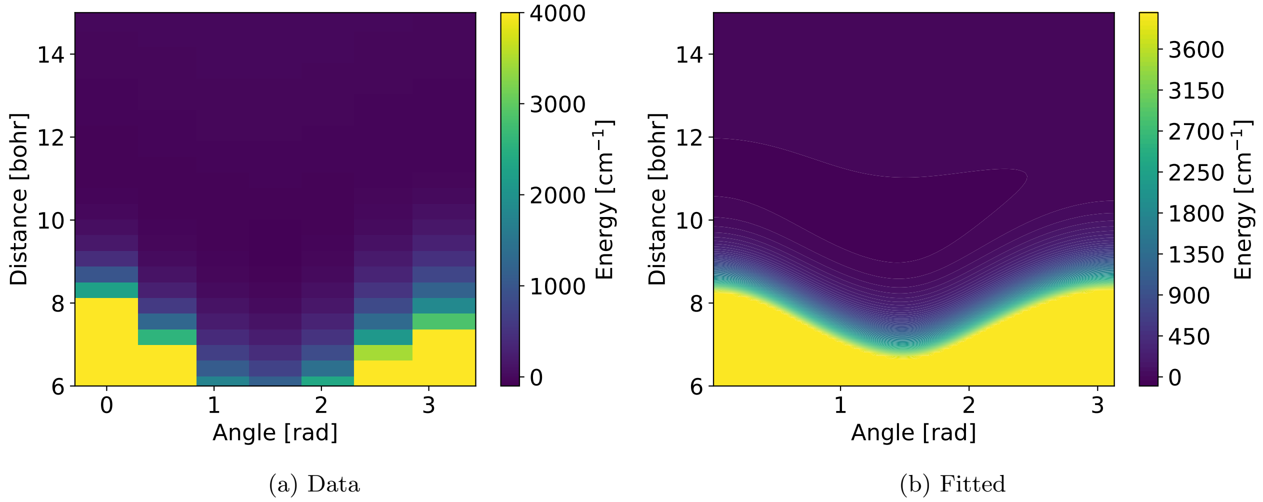


Figure 1: Fitting of intermolecular potential

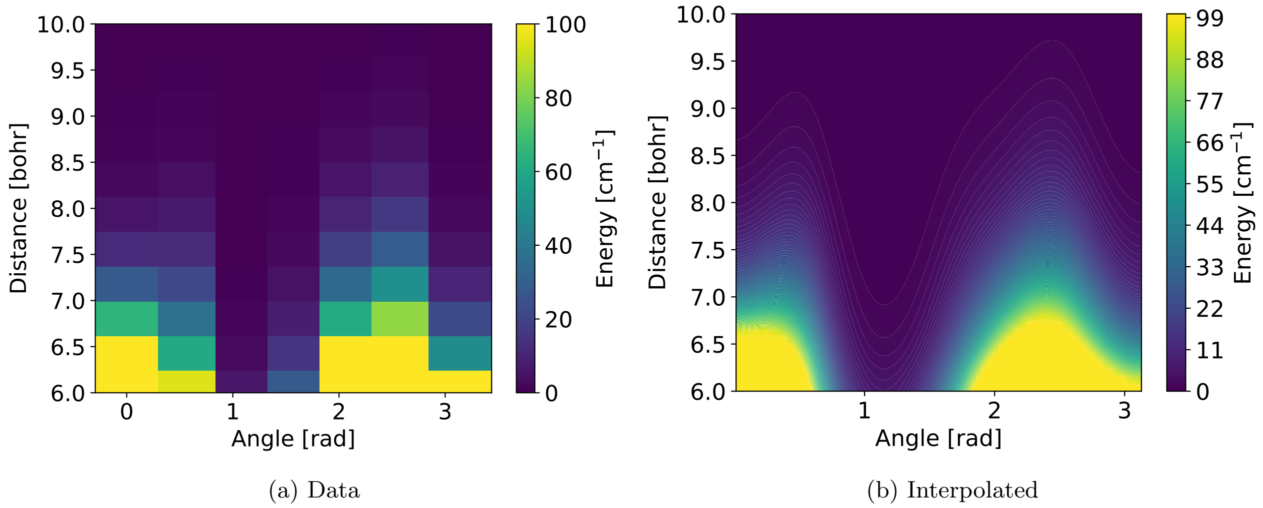
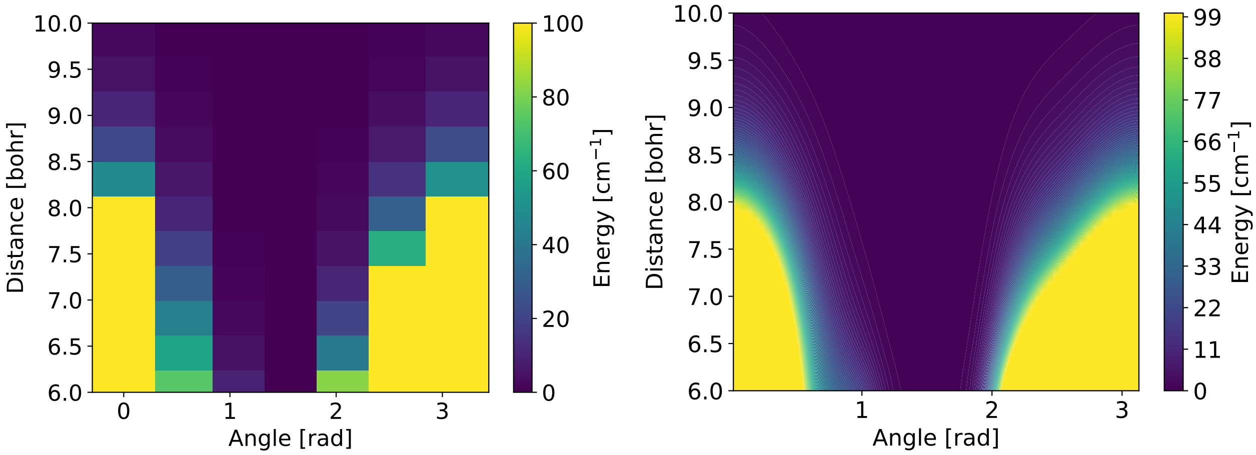


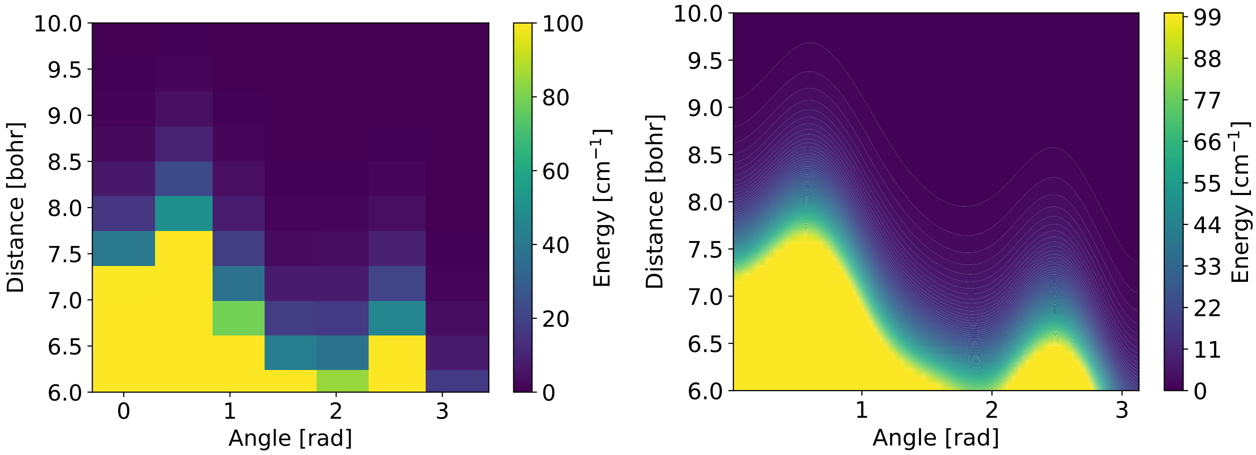
Figure 2: Interpolation of $X\Pi$ gamma potential



(a) Data

(b) Interpolated

Figure 3: Interpolation of $B\Sigma$ gamma potential



(a) Data

(b) Interpolated

Figure 4: Interpolation of $A\Pi$ gamma potential

2 Truth tests for coriolis effect

Comparison of the ground state of the system defined by the space-fixed Hamiltonian

$$\hat{H} = -\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{\hat{L}^2}{2\mu R^2} + V(R,\theta), \tag{1}$$

with our system in body-fixed frame for which we make rotational constant $B = 0$ and the Hamiltonian is

$$\hat{H} = -\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{(\hat{J}-\hat{j})^2}{2\mu R^2} + V(R,\theta). \tag{2}$$

The conserved quantities for the first system is the angular momentum projection number m_l, in case of the body-fixed frame the conserved quantity is the total angular momentum J.

In the case of harmonic oscillator potential

$$V(r,\theta) = \frac{\mu\omega^2}{2}(r - r_0)^2. \tag{3}$$

The calculated ground state of the space-fixed Hamiltonian is then ω for $m = 0$. For the body-fixed Hamiltonian the calculated ground state for $J = 2$ is also ω with coriolis effect and 1.15ω if we neglect coriolis effect.

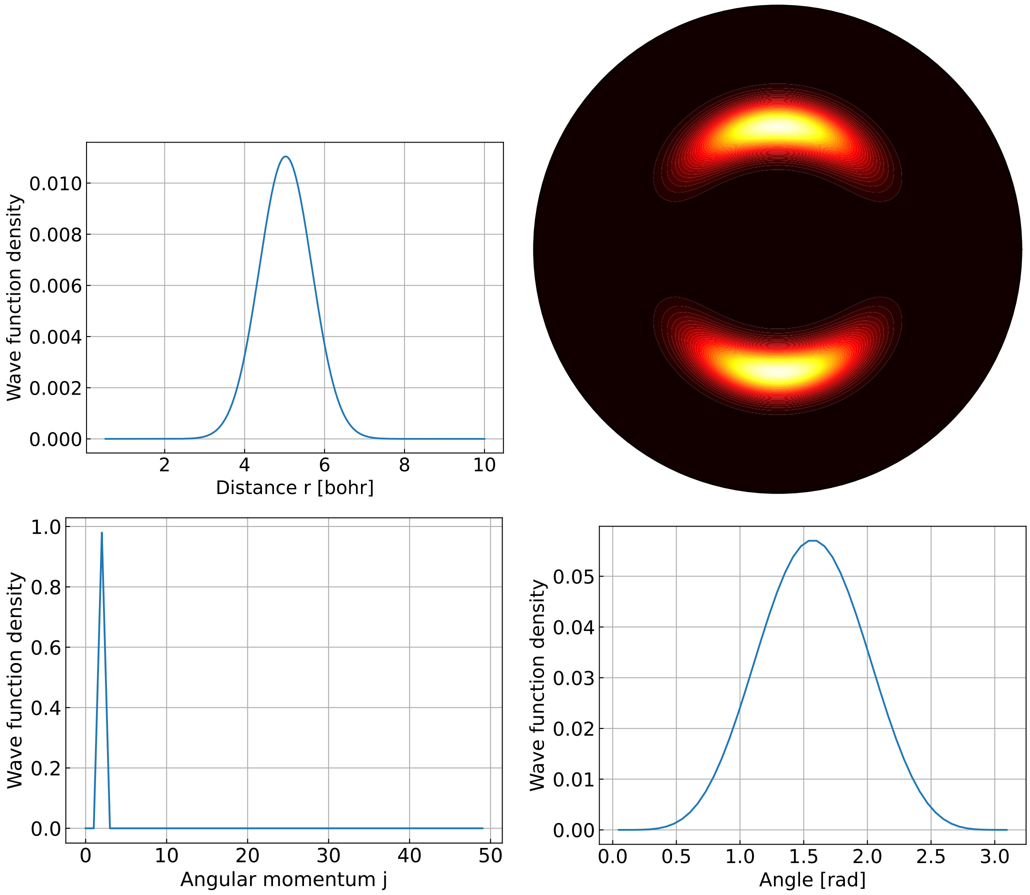


Figure 5: Wave function calculated ground state for $J = 2$ without coriolis effect.

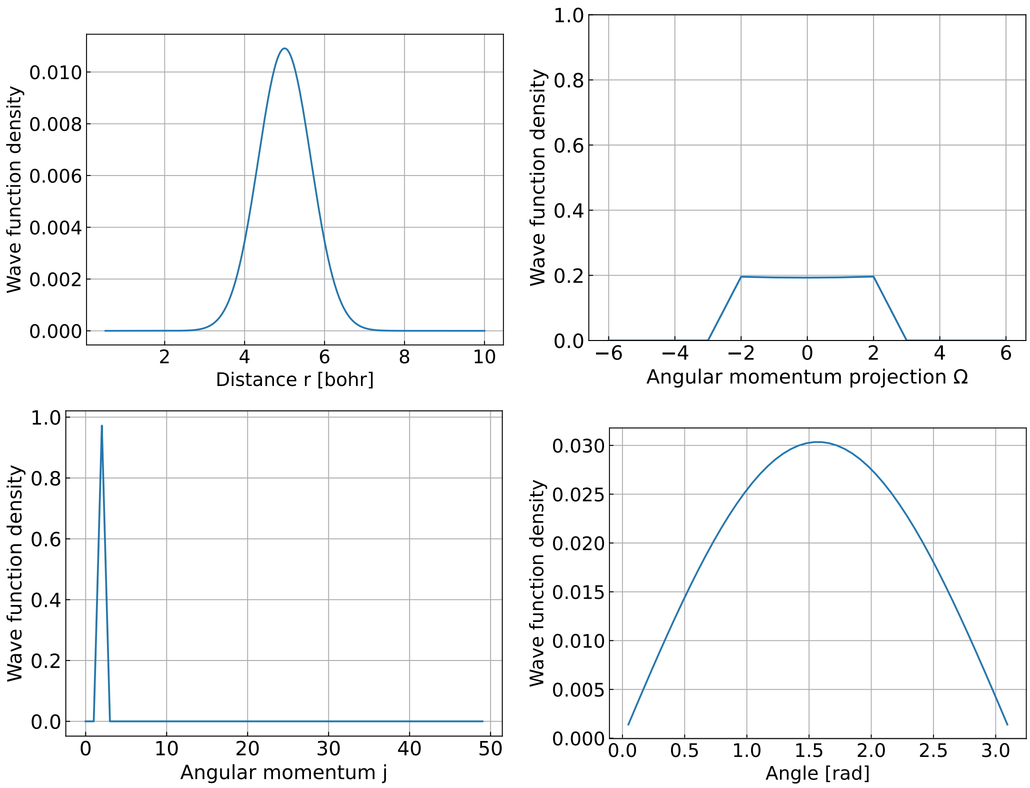
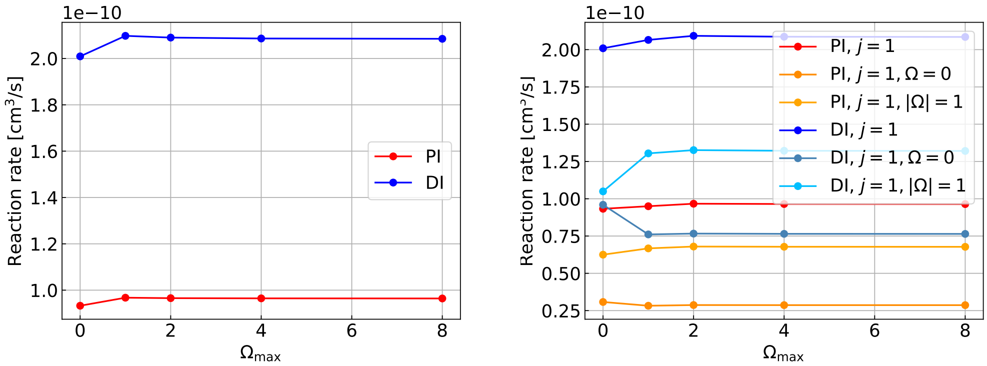


Figure 6: Wave function calculated ground state for $J = 2$ with coriolis effect.

For potential of the form $V(r, \theta, \phi)$ the space-fixed Hamiltonian doesn't have any conserved angular numbers, however in body-fixed frame we have still J conserved. It can be deduced that in the case of $B = 0$, J gives additional infinite degeneracy, because of that for every conserved J the ground state is ω, however only after the inclusion of coriolis effect.

3 Reaction rate dependence on coriolis effect body-fixed projection cutoff

Animations of collisions with high Ω_{max} showed that the mixing of total projection is up to $\Omega = 45$. However reaction rate calculations converge for $\Omega_{\mathrm{max}} = 2$, convergence test is shown below.



(a) Reaction rate for $j = 0$.

(b) Reaction rate for $j = 1$.

Figure 7: Calculated reaction rates dependence on Ω_{max}.

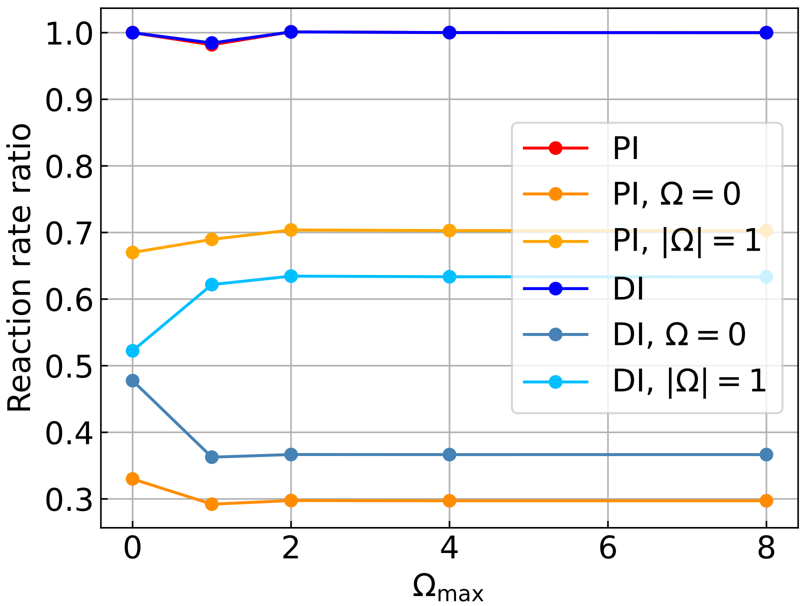
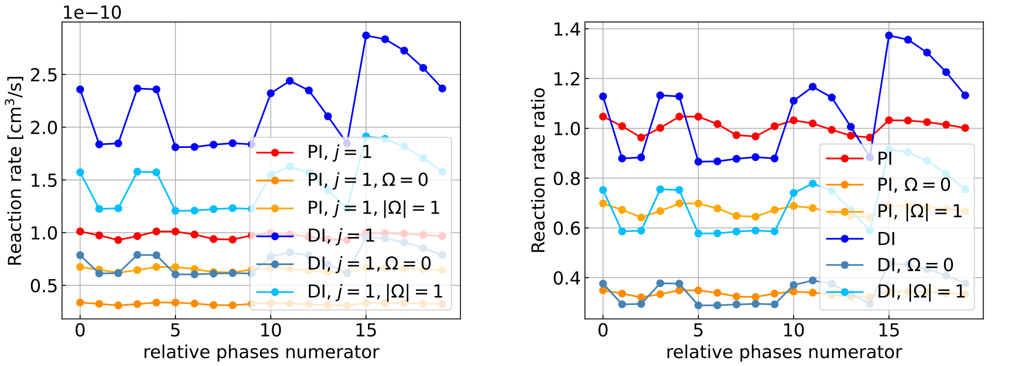


Figure 8: Calculated reaction rate ratio between $j = 1$ and $j = 0$, dependence on Ω_{max}.

For the initial state $j = 1$ being the superposition of initial projections

$$|\psi\rangle = \frac{1}{3}\left(e^{i\phi_{-1}}\left|-1\right\rangle + \left|0\right\rangle + e^{\phi_1}\left|1\right\rangle\right), \qquad (4)$$

the reaction rate for different initial relative phases is shown below.



(a) Reaction rates for $j = 1$ for different phases. (b) Reaction rate for $j = 1$ for different phases

Figure 9: Calculated reaction rates dependence for different phases.

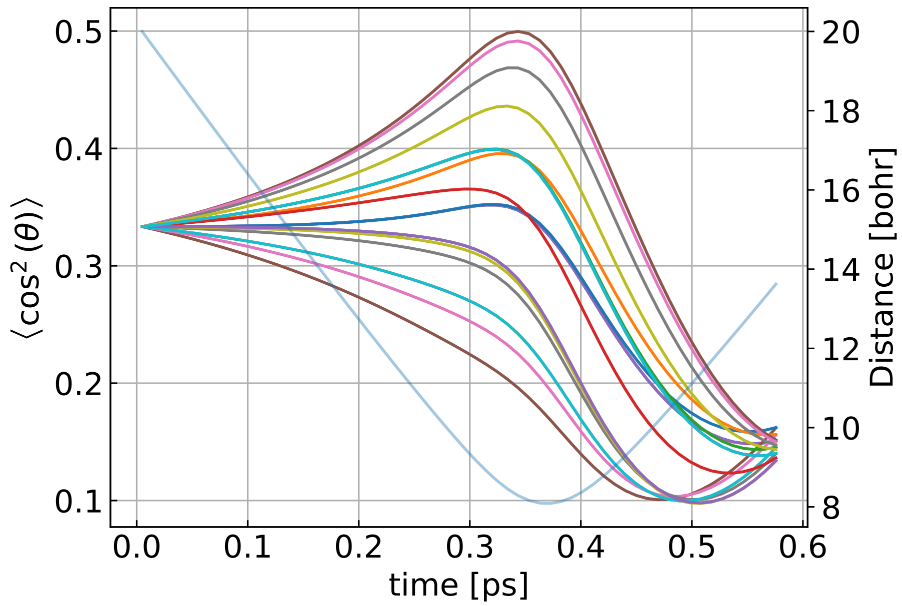


Figure 10: Calculated alignments during the collision for different relative phases.

4 Reaction rate ratios for force field scalings

Scaling the parameters of the force field did not change the reaction rate ratio from value of 1.