This SOAR project is a continuation of an ongoing research effort to model changes in quantum rotational energy levels \( j \) of NaK molecules that undergo collisions with helium (He). Experimental results at Lehigh University showed a propensity for even \( j \) transitions. Previous theoretical research on this project completed at Lehigh University did not account for vibration of the NaK molecule. This project demonstrates a need for including the NaK vibrational motion. The next stage included an approximation using weighted averages of multiple Potential Energy Surfaces (PES's) to map the He interaction with an NaK molecule over the range of internuclear separations of Na and K corresponding to the vibrational state. This yielded results that qualitatively matched the experimental observations and made it clear that vibration played a crucial role in the interactions. The goal of this SOAR project was to prepare to include vibrational motion of NaK into scattering calculations by fitting PES at a range of NaK separations with continuous functions. Each individual PES was fit with a linear combination of functions. The coefficients of these functions for each discrete value of internuclear separation were interpolated. These new fits of the PES's allow for scattering calculations with vibrational effects included.

**Introduction**

This project focuses on the system of particles depicted in Fig. 1 where Na is bonded with K in a molecule and He is on a collision trajectory with the NaK. This is a Jacobian coordinate system originating from the Center of Mass of the NaK where \( R_g \) is the radial distance of He from the origin, \( r \) is the internuclear separation of the NaK and \( \theta \) is the angle between \( R_g \) and \( r \).

![Fig. 1 Jacobian Coordinate System with parameters \( R_g \), \( r \), and \( \theta \).](image)

Initial research was conducted approximating the NaK as a rigid rotor by fixing the coordinate \( r \) at the NaK equilibrium distance. Following this method, a weighted average over the molecule's vibrational separation was implemented which supported that vibration played a crucial role in the interaction with He. However, the results we wanted. To improve the efficiency of fitting the PES's, the authors tried fitting the coefficients as a function of \( R_g \) and \( r \) using the tspliner program. This project was a continuation of ongoing research efforts to model changes in quantum rotational energy levels \( j \) of NaK molecules that undergo collisions with helium (He). The General Atomic and Molecular Electronic Structure System program (GAMESS) was used to calculate the potential energy surface (PES) for NaK. The results at Lehigh University showed a propensity for even \( j \) transitions. This project focuses on the system of particles depicted in Fig. 1 where Na is bonded with K in a molecule and He is on a collision trajectory with the NaK. This is a Jacobian coordinate system originating from the Center of Mass of the NaK where \( R_g \) is the radial distance of He from the origin, \( r \) is the internuclear separation of the NaK and \( \theta \) is the angle between \( R_g \) and \( r \).

![Fig. 2 Rate constant \( k \) of NaK transitioning from the initial rotational state \( j=14 \) to a final state \( j' \). Most NaK remains in the \( j=14 \) so this result is omitted from the figure.](image)

Dynamic scattering calculations were performed using the Multi-Channel Time Dependent Hartree MCTDH program. The scattering method involves propagating a wavepacket representing the He atom toward a Potential Energy Surface (PES) which represents the NaK. The General Atomic and Molecular Electronic Structure System program (GAMESS) was used to calculate the potential energy of the He interaction with the NaK over a grid of positions of \( R_g \) and \( \theta \), similar to that shown in Fig. 3. The original work fixed the \( R_g \) value at the NaK equilibrium position. Then to create the final PES, the PES could be represented in MCTDH as the separable function:

\[
V(R_g, \theta) = \sum_{j} \langle \theta \rangle P_j(R_g) \cos(\theta j)
\]

where \( P_j(R_g) \) are Legendre Polynomials and \( \theta j \) is the coordinate \( \theta \) in the coordinate \( j \).

![Fig. 3 Example diagram of GAMESS point calculations.](image)

The improved qualitative match of the weighted average approximation confirmed that vibration plays a crucial role in the changes of rotational state caused by the collisions. To incorporate the \( R_g \) dependence into the scattering calculations, we must interpolate the coefficients \( \langle \theta \rangle P_j(R_g) \) over values of vibrational separation \( r \). This project focuses on the system of particles depicted in Fig. 1 where Na is bonded with K in a molecule and He is on a collision trajectory with the NaK. This is a Jacobian coordinate system originating from the Center of Mass of the NaK where \( R_g \) is the radial distance of He from the origin, \( r \) is the internuclear separation of the NaK and \( \theta \) is the angle between \( R_g \) and \( r \).

![Fig. 4 Side by side example of 3D PES and a 2D projection.](image)

![Fig. 5 Results of the rigid rotor model showing the rate constant of \( j = 14 \rightarrow j' \) transitions vs \( j' \) plotted along with experimental results.](image)

The final interpolated PES is shown in Fig. 4.

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![Fig. 6 The probability densities of the vibrational states \( \nu = 0 \) and \( \nu = 16 \) as a function of \( r \).](image)

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![Fig. 7 Example of manual polynomial fits of Taylor expansion coefficients as a function of \( R_g \).](image)

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![Fig. 8 Example of spline fits for \( R_g \) and all derivatives of the potential in a single plot.](image)

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![Fig. 9 Example of manual polynomial fits of Taylor expansion coefficients as a function of \( R_g \).](image)

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![Fig. 10 Example of manual polynomial fits of Taylor expansion coefficients as a function of \( R_g \).](image)

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![Fig. 11 Example of manual polynomial fits of Taylor expansion coefficients as a function of \( R_g \).](image)