Testing a Conjecture about a Kinematics Limit in Molecular Physics

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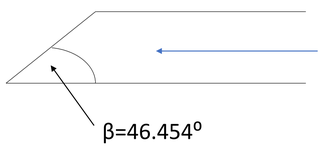
Background

- In collisions between a diatomic molecule and a atom, a given amount of energy transfer can occur or a change to the internal energy of the molecule can occur, populating quantum states of vibrational and rotational energy. The energy available to a collision is given by:

$$E_{avail} = E_{trans} + \varepsilon(V,J)$$

- We study the conjecture first published by the Valentini group (Picconatto et al. in 2001), which shows that in reactive collisions, the maximum rotational state is never populated.
  - From a theoretical perspective, if a molecule populated the maximum rotational state for the total energy, all of the translational energy in the system would be lost, and the particles would never separate.
- This work looks at non-reactive collisions such as Li_2+Xe instead, addressing a question not directly considered in the original work.
- For the Li_2+Xe collision, we analyze the effect of changing the initial energy on the maximum expected vs actually populated rotational state.
- Picconatto introduces a model for the total internal energy available where the total energy is scaled by a "skew angle", an angle in a two-dimensional representation of an atom-molecule potential energy surface (shown below for the Li_2+Xe system).



- For the Li_2+Xe system, the skew angle is 46.454°. A collision can be represented by a line entering the surface at a given angle, and the changes in energy are shown through the reflection of the line against the walls of the box. The line bounces off of the skewed wall, and populates different j and v states.

Methods

Simulation of Trajectories

- We carry out a Monte-Carlo simulation of the collision dynamics using the fast action-angle algorithm devised by Neil Smith in order to simulate batches of trajectories based on a set of initial conditions.
- We vary the relative collision speed of the system in order to vary the total energy of the system.
- We use the Peterson-McBane Li_2+Xe *ab initio* potential to perform these calculations, and then determine the highest-populated rotational state from our computational data.
- From there, we calculate the expected maximum rotational state based on a statistical model, along with the expected maximum rotational state based on the model proposed by Picconatto et. al..
- We are then able to perform surprisal analysis on our results to find the deviation of our experimental/simulated data from a prior statistical model.

Results

TABLE III. $H+H_2 \rightarrow H_2+H$.

Reaction (E_{trans})	$j'_{max,meas.}$	$j'_{max,model}$	$j'_{max}(E_{avail})$
$H+D_2$ (1.3 eV)[a]			
$v'=0$	15	14	16
$v'=1$	12	11	13
$v'=2$	8	7	9

Table 1 (Above): A chart from the Picconatto paper depicting a collision, and the maximum populated final J state three ways: experimentally, calculated through their model, and with the maximum energy available.

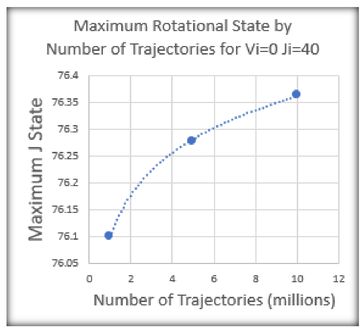


Figure 1 (Right): A comparison of the maximum populated rotational state to the number of trajectories performed.

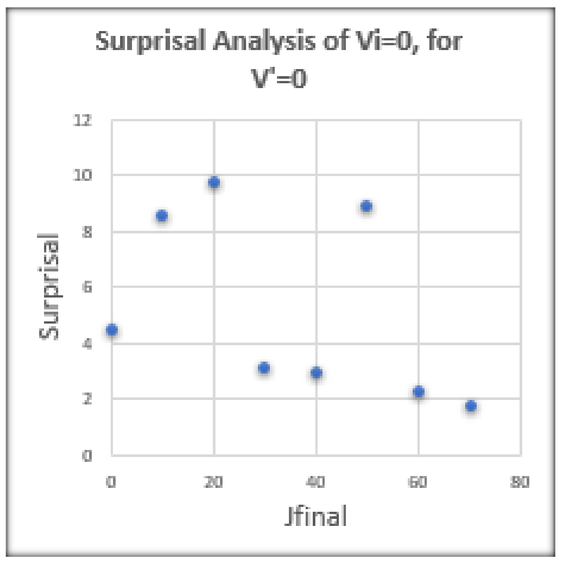


Figure 2 (Above)

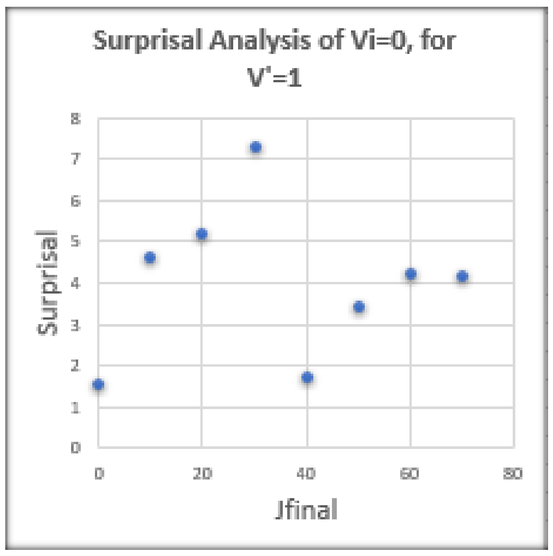


Figure 3 (Below)

Li_2+Xe Reaction, v_i=0, j_i=10			
	$j_{max,\ measured}$	$j_{max,\ Picconatto\ Model}$	$j_{max,\ E_{avail}}$
v'=0	65.02	56.50	72.14
v'=1	63.50	51.65	68.35

Li_2+Xe Reaction, v_i=0, j_i=20			
	$j_{max,\ measured}$	$j_{max,\ Picconatto\ Model}$	$j_{max,\ E_{avail}}$
v'=0	67.16	59.34	74.52
v'=1	65.51	54.73	70.85

Li_2+Xe Reaction, v_i=0, j_i=30			
	$j_{max,\ measured}$	$j_{max,\ Picconatto\ Model}$	$j_{max,\ E_{avail}}$
v'=0	70.88	63.79	78.32
v'=1	68.68	59.51	74.82

Li_2+Xe Reaction, v_i=0, j_i=40			
	$j_{max,\ measured}$	$j_{max,\ Picconatto\ Model}$	$j_{max,\ E_{avail}}$
v'=0	76.3639	69.5601	83.3609
v'=1	74.2940	65.6316	80.0628

Table 2 (Above)

- **Figure 1** depicts how maximum final rotational state based on the number of trajectories simulated begins to converge at j=76.4 after 10 million trajectories.
- **Table 2** shows the maximum j values for our simulated collision. The first column represents the change in vibrational state, the second is the highest populated j state in our simulations, the third is the highest populated j state using the Picconatto model, and the fourth is the highest populated j state just considering the total energy. We format it this way to compare with the data compiled by Picconatto in **table 1.**
- Within **table 2**, we can see that the Valentini conjecture holds true–the simulated trajectories never populate states as high as the maximum state suggests that it could. However, their proposed model stays far under the maximum simulated rotational state for all of the data.
- Surprisal analysis shows how much dynamical information is contained within the experimental data, as opposed to how much information is purely statistical. To perform it, we compare our data with a model of the probability of certain events happening. In our case, we compare the probability of finding the maximum j experimentally with the probability of finding it using the Rigid Rotor Harmonic Oscillator model of molecular collisions.
- **Figures 2 and 3** each show the results of surprisal analysis being performed on different sets of data. Our surprisal analysis shows that the experimental data does not especially cohere to the model that we use–the surprisal is generally high, which indicates a large deviation from the data. However, the surprisal does not seem to follow any notable trends.

Conclusions

- First, it is notable that an increase in the number of simulated trajectories does not increase the maximum populated j_{final} linearly. Instead, it begins to converge to a specific maximum j. We can reasonably say that after 10 million trajectories run, we can get the maximum j to 4 significant digits.
- Second, it seems that the model proposed by Picconatto et. al. does not hold up for non-reactive molecular collisions, at least with the system that we study. Further work will be necessary to explore whether this is true for other non-reactive systems.
- Finally, when we perform our surprisal analysis, we use the RRHO model to obtain our prior distributions. While this makes sense for the point we are at right now in the work, it will be important moving forward to create an even better model to obtain prior distributions.

References

R. D. Levine and J. L. Kinsey, "Information Theoretic Approach to Collisions", in *Atom-molecule Collision Theory: a Guide for the Experimentalist*, R. B. Bernsetin, ed., Plenum, 1979

Mahan, Bruce H.. "Collinear collision chemistry: I. A simple model for inelastic and reactive collision dynamics." *Journal of Chemical Education* **51** (1974): 308.

Carl A. Picconatto, Abneesh Srivastava, James J. Valentini; Reactions at suprathreshold energy: Evidence of a kinematic limit to the internal energy of the products. J. Chem. Phys. 22 January 2001; 114 (4): 1663–1671. https://doi.org/10.1063/1.1333706

Neil Smith; On the use of action-angle variables for direct solution of classical nonreactive 3D (Di) atom–diatom scattering problems. *J. Chem. Phys*. 15 August 1986; **85** (4): 1987–1995. https://doi.org/10.1063/1.451142

N. Smith, *Journal of Chemical Physics* **85**, 1987 (1986).

I would like to thank the QAC for giving me this opportunity to do summer research. In addition, I'd like to thank my labmates: Mathis, Othmane, Jimmy, and Denuwan, without whom I couldn't have done this research. Finally, I'd like to thank Henk Meij, who monitors the High-Performance Computing Cluster at Wesleyan.