Using an Autoencoder for Dimensionality Reduction in Quantum Dynamics

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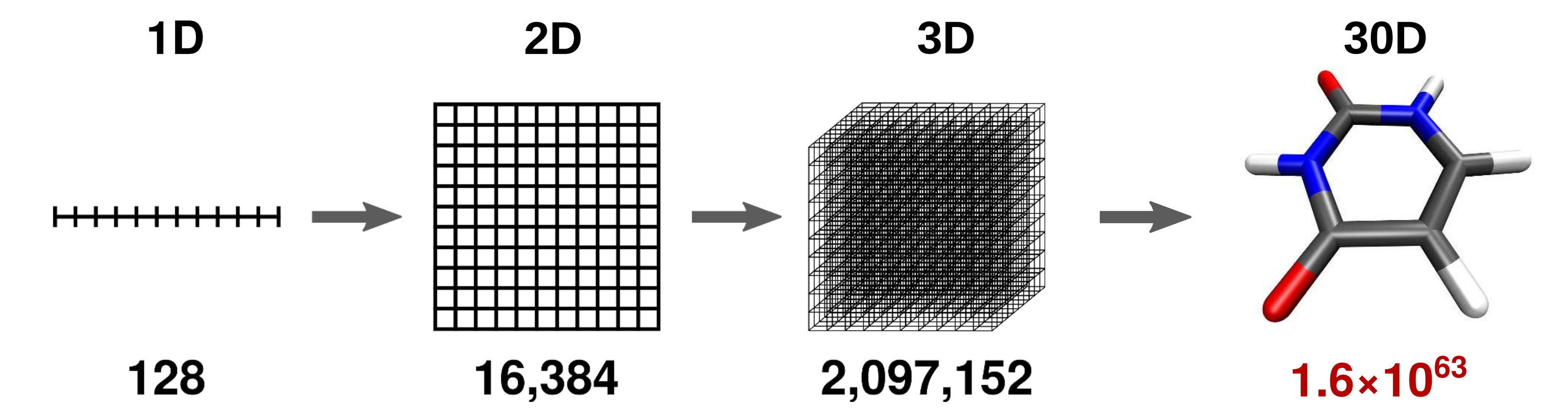
Abstract

Quantum dynamics is an important tool in the investigation of ultrafast (photo)chemical processes. The time-dependent Schrödinger equation is solved on a discrete spatial grid of nuclear coordinates. One of the main limitations of this approach is the exponential scaling of the number of grid points with the dimensionality. The use of coordinate reduction techniques is therefore crucial. Non-linear coordinates are of special interest in this context, since they can typically cover the same reactive space as linear coordinates (e.g. normal modes) in fewer dimensions.

We present a machine-learning workflow [1] to construct such non-linear reduced dimensional subspaces. The first step is to sample the configuration space of the desired reaction pathway with semiclassical trajectories. The obtained data set of molecular structures can be used as input to an autoencoder network to find non-linear coordinates. As first examples we focus on proton transfer reactions in organic molecules, both in the ground state as well as in excited states.

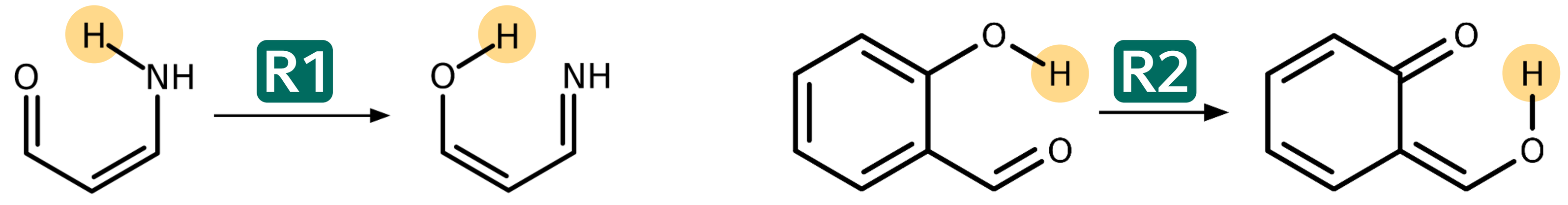
The Curse of Dimensionality



- Number of grid points scales exponentially with number of dimensions
- Coordinate reduction is mandatory for grid based quantum dynamics
- Selection of reactive coordiantes usually rely on human intuition

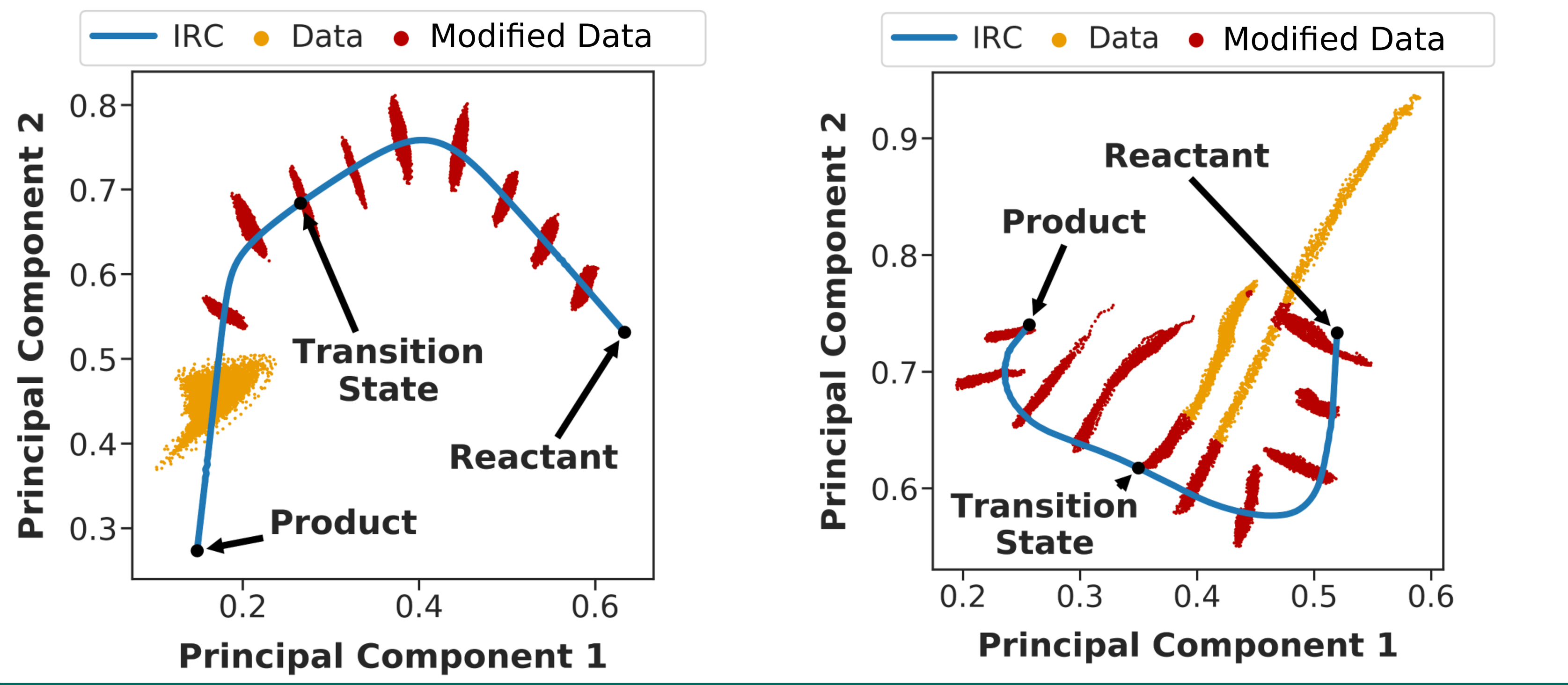
Dataset Generation Workflow

- Run semiclassical trajectories orthogonal to the intrinsic reaction coordinate (IRC)
- Remove redundancy by enforcing a minimum distance between data points
- Remove translation and rotation via Eckart conditions
- Remove bias towards one energy minimum by selectively removing data clusters

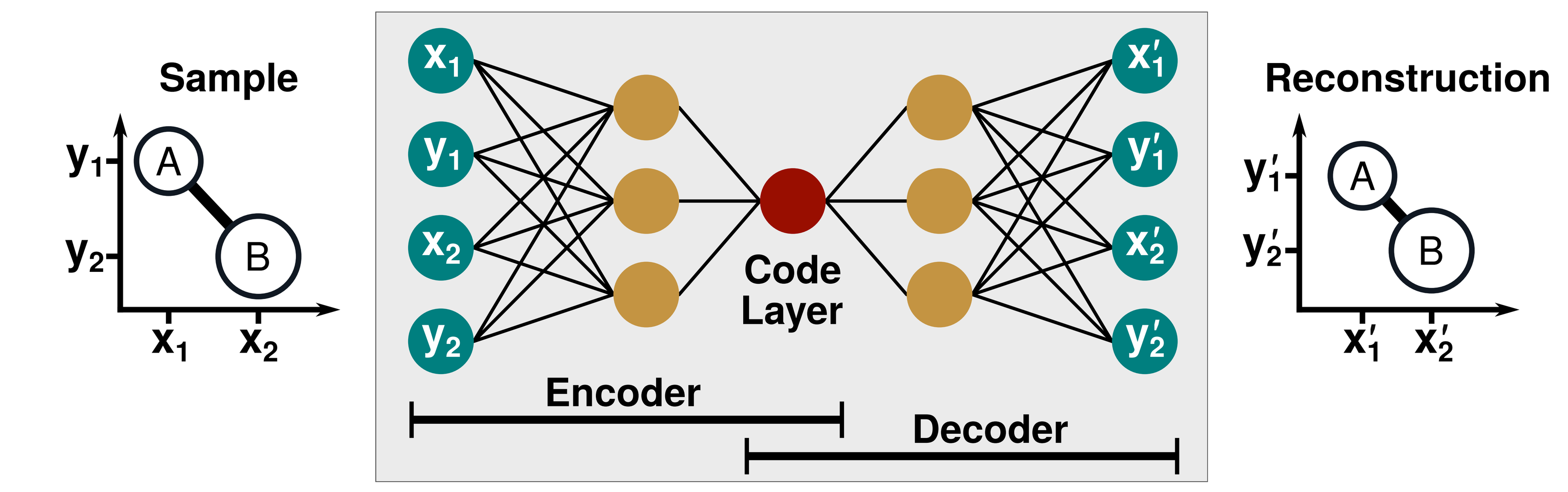


500 trajectories à 500 fs in S_0

500 trajectories à 200 fs in S_1

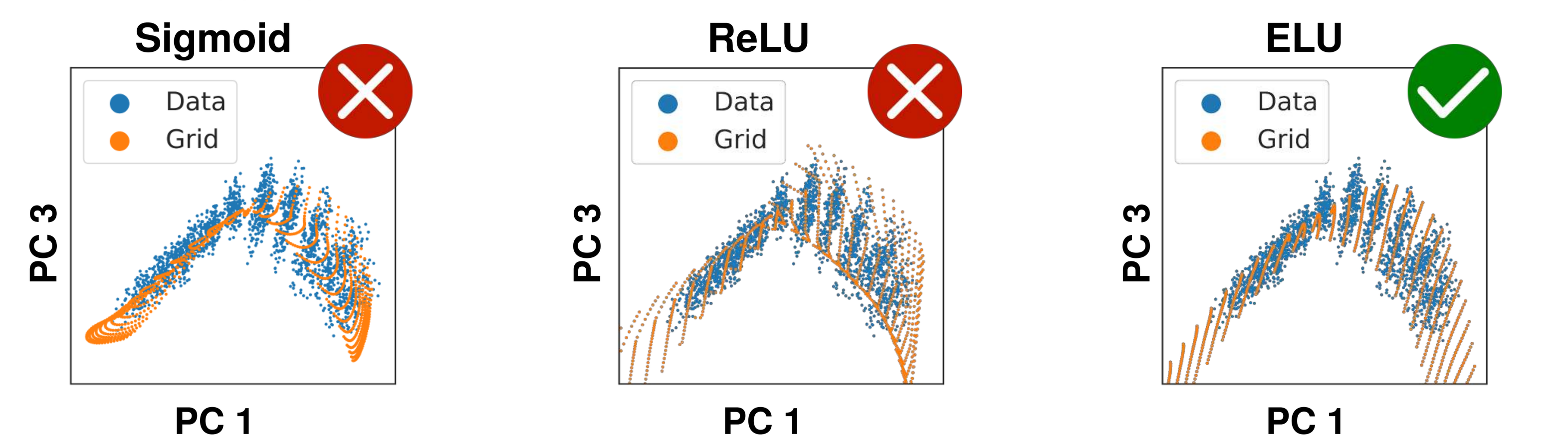


Reactive Coordinates from an Autoencoder

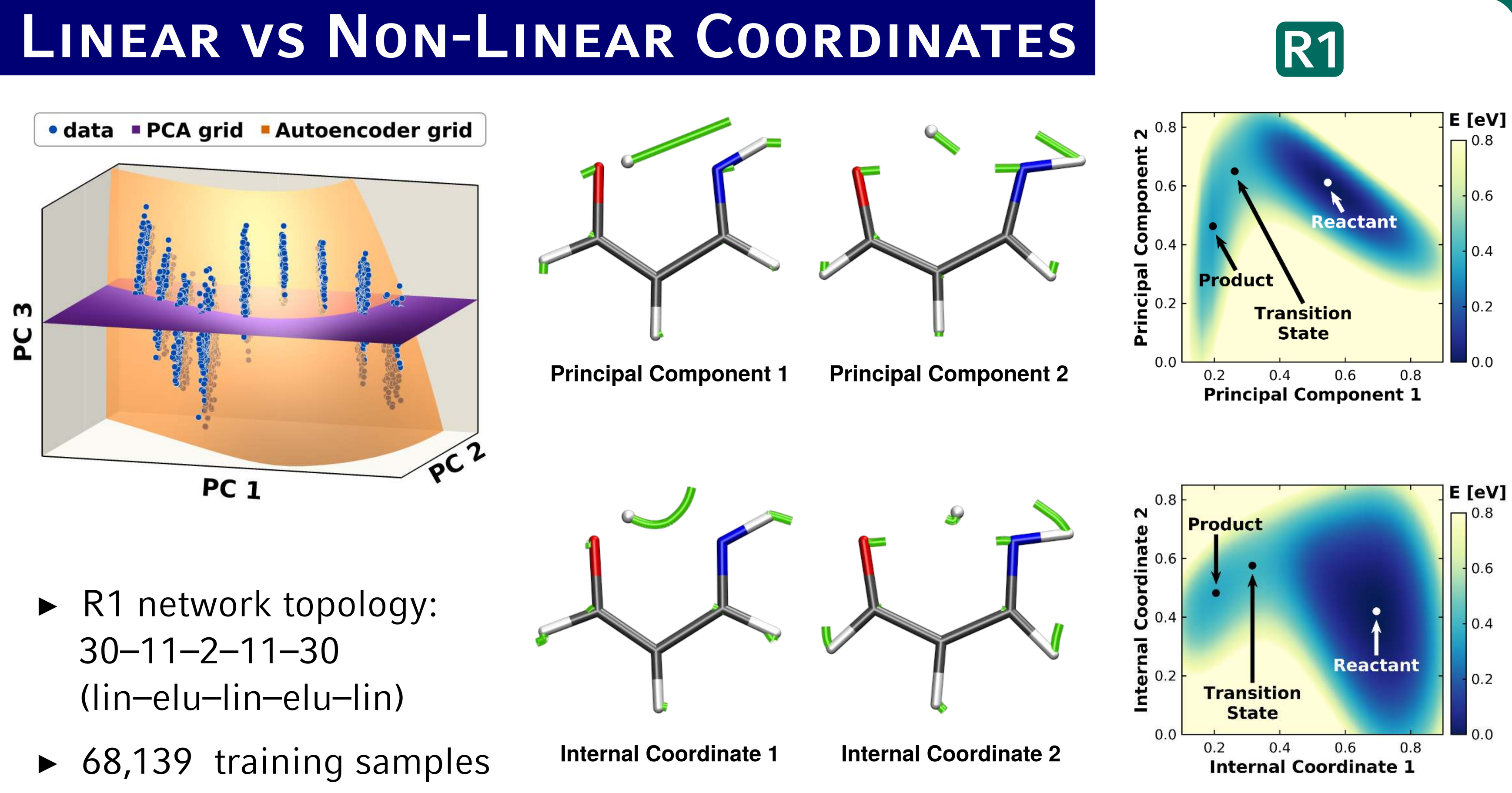


- Autoencoder: artificial neural network with bottleneck architecture
- Learn low-dimensional, non-linear representation of input data
- Trained network is used to construct a grid inside the non-linear subspace
- Final grid must be approximately equispaced to allow evaluation of the kinetic energy operator in the G-matrix formalism [2-5]

  → Choose appropriate activation functions



Linear vs Non-Linear Coordinates



- R1 network topology: 30–11–2–11–30 (lin–elu–lin–elu–lin)
- 68,139 training samples

Energies of Critical Points

- Non-linear grids cover the data much better and are capable of recovering full-dimensional energy differences (DFT/B3LYP/cc-pVTZ)

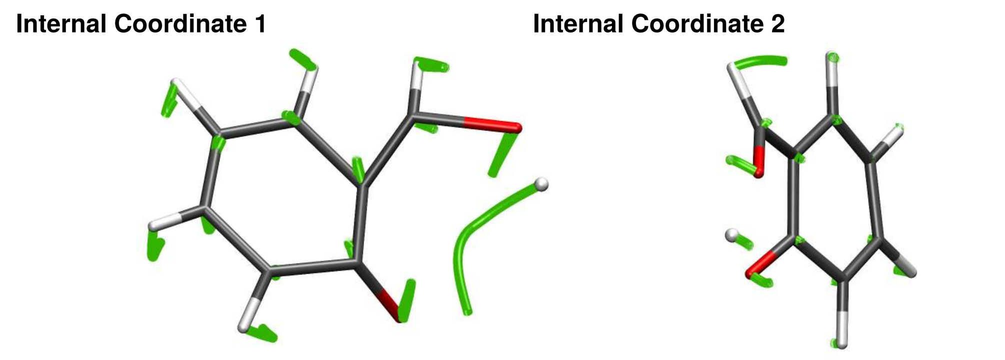
Coord.	ΔE_{min} [eV]	ΔE_{TS} [eV]
Linear	0.33	0.40
Non-linear	0.36	0.40
Full-Dim.	0.34	0.42

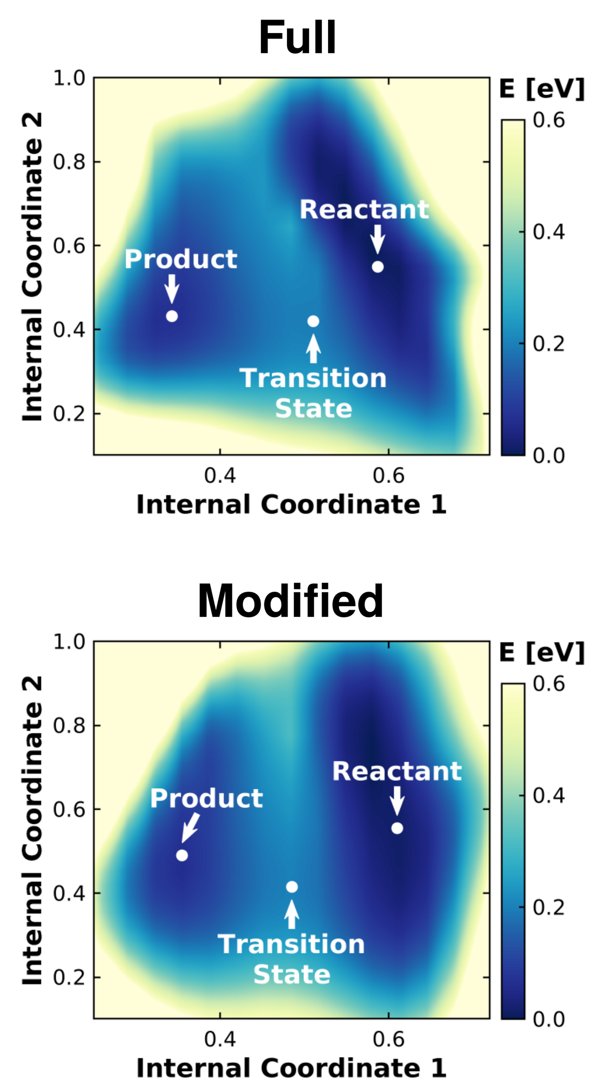
Effects of Dataset Modification

- Training on the full data set can induce (too) strong non-linearities in the grid
- Improvements through manual data modification?
- R2 network topology: 45–12–2–12–45 (lin–elu–lin–elu–lin)
- TD-DFT/M06-2X/cc-pVTZ

Training Success

	R1 Full	R1 Modified	R2 Full	R2 Modified
Samples	85,305	68,139	13,756	11,720
Epochs	100	100	80	50
Accuracy [%]	88	82	86	96





Energies and Structures of Critical Points

R2 Data	ΔE [eV] Minima	ΔE [eV] Barrier	RMSD [Å] Reactant	RMSD [Å] TS	RMSD [Å] Product
Full	0.071	0.20	0.14	0.16	0.23
Augmented	0.064	0.20	0.15	0.15	0.22
Full-Dim.	0.072	0.20	–	–	–

References

[1] J. P. P. Zauleck, R. de Vivie-Riedle, *J. Chem. Theory Comput.* **14**, 55-62 (2018).
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[5] J. P. P. Zauleck, S. Thallmair, R. de Vivie-Riedle, arXiv: 1712.10170v1 (2017).

Further Information

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