

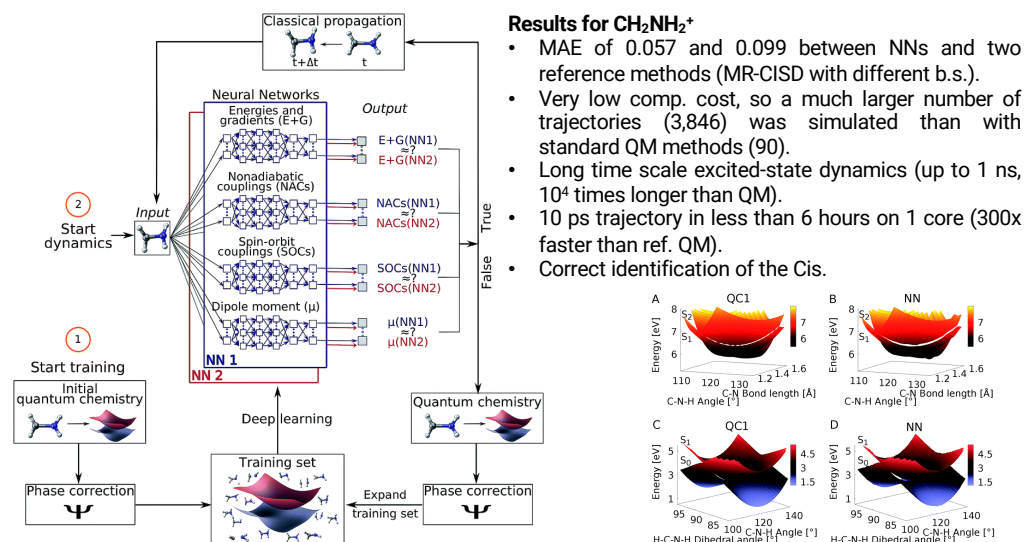
[1] Long timescale surface hopping dynamics with deep NNs

SHARC with multi-layer feed-forward NNs

- Use NNs instead of QM calculations to predict energies, gradients, couplings and dipole moments
- Relationships between the nuclear coordinates and the corresponding electronic properties are learned from a training set

Training set generation and adaptive sampling for excited states

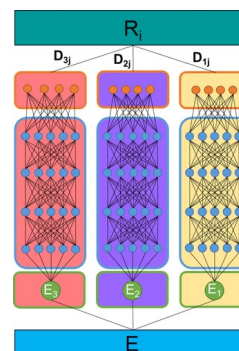
- Each data point is one set of nuclear coordinates and its associated set of quantities computed with a reference method.
- Initial training set based on normal mode scans and then switch to an **adaptive sampling** scheme that automatically identifies untrustworthy regions not covered by the initial training set.
- Whenever the different NNs make different predictions, the corresponding geometry is assumed to lie in a conformational region with too few training points → expand the training set by computing the quantum chemistry data for this geometry.
- During the run, threshold for the error between the NNs is adapted ($\times 0.95$) until the conformational space is sampled to make accurate predictions without any reference calculation.



[2] Pure deep learning vs. *ab initio* non-adiabatic excited state dynamics

Feed-forward deep NNs with Zhu-Nakamura TSH method for pure ML non-adiabatic dynamics

- Aim: explore topology of S₀ and S₁ PESs and the S₀/S₁ conical intersection of CH₂NH.
- DNNs model where PES of the molecule is expressed as sum of energies of constituent atoms.



⇐ Schematic model of the DNNs: 4 hidden layers, 3 atoms.

Atom coordinates R_i are transformed into a set of input vectors D_{ij} .

Parameters of the DNNs for an atom are optimised iteratively

$$\text{Energies as: } E = \sum_i E_i \quad \text{with} \quad E_i = \mathbb{F}_i^{\text{out}}[\mathbb{F}_i^{\text{out}}[\mathbb{F}_i^{\text{out}}[\dots(\mathbb{F}_i^{\text{out}}(\{d_i^0\}))]]]]$$

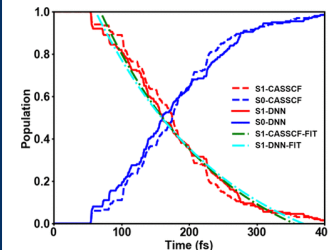
Two individual DNN models trained independently for both S₁ and S₀ PESs of CH₂NH on CASSCF data calculated for the same set of molecular coordinates.

Final DNN models are trained on 90,000 *ab initio* data points prepared using molecular dynamics simulations.

S₀ and S₁ energy profiles calculated from the trained DNN models fully overlap with CASSCF.
S₁/S₀ CI topology well reproduced (see 2D and 3D PES ⇒)

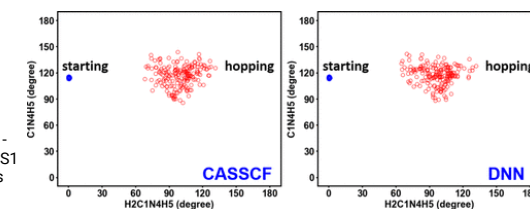
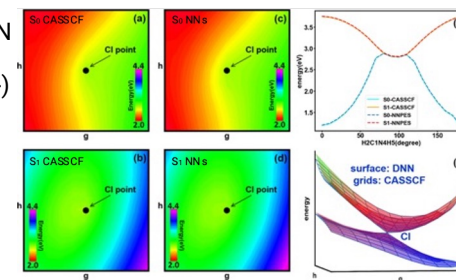
Results for DNNs

- S₁-S₀ gap same well reproduced at all hopping and Franck-Condon regions
- TD S₀ and S₁ populations match *ab-initio* ones
- S₁ to S₀ hopping starts at same time (55 fs)
- Similar distribution of hopping points



TD state population over 200 trajectories

Distributions of the bending \angle C1-N4-H5 and dihedral \angle H2-C1-N4-H5 angles at the S₁ → S₀ hopping points



References and figures: [1]: Reprinted from *Chem. Sci.* **2019**, *10*, 8100 under CC-BY OA license. [2]: Reprinted with permission from *J. Phys. Chem. Lett.* **2018**, *9*, 6702 © 2018 ACS.