

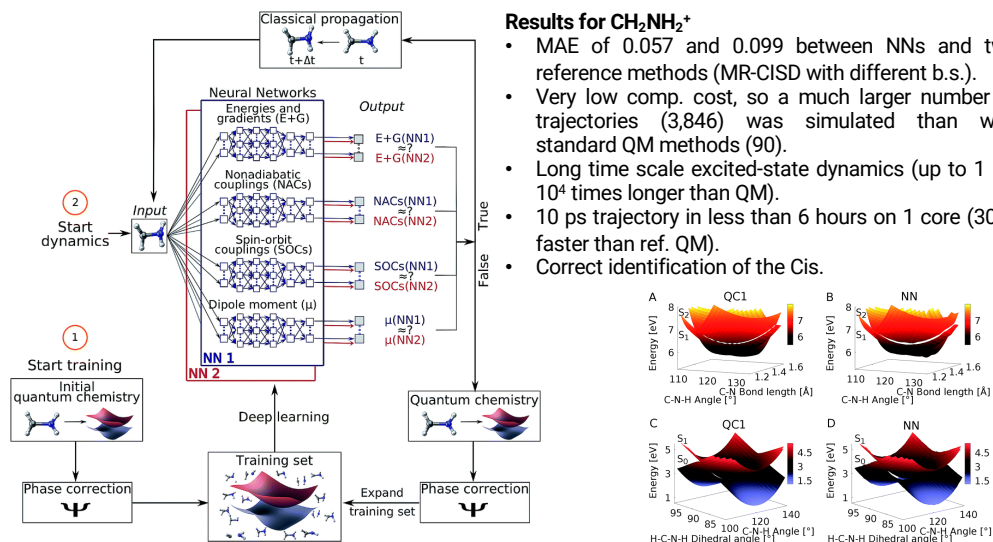
[1] Long timescale surface hopping dynamics with deep NNs

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

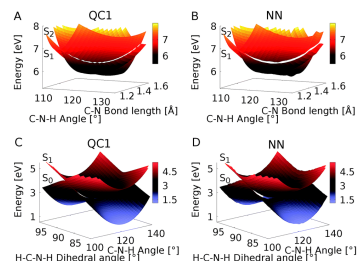
Training set generation and adaptive sampling for excited states

- 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.



Results for CH_2NH_2^+

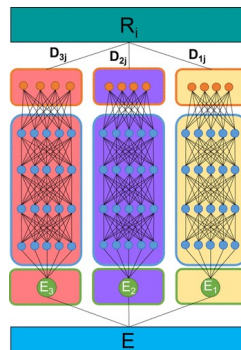
- MAE of 0.057 and 0.099 between NNs and two reference methods (MR-CISD with different b.s.).
- Very low comp. cost, so a much larger number of trajectories (3,846) was simulated than with standard QM methods (90).
- Long time scale excited-state dynamics (up to 1 ns, 10^4 times longer than QM).
- 10 ps trajectory in less than 6 hours on 1 core (300x faster than ref. QM).
- Correct identification of the Cis.



[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 S_0 and S_1 PESs and the S_0/S_1 conical intersection of CH_2NH .
- 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} .

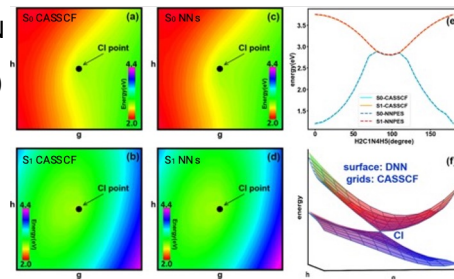
Parameters of the DNNs for an atom are optimised iteratively

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

Two individual DNN models trained independently for both S_1 and S_0 PESs of CH_2NH 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.

S_0 and S_1 energy profiles calculated from the trained DNN models fully overlap with CASSCF. S_1/S_0 CI topology well reproduced (see 2D and 3D PES ⇨)



Results for DNNs

- S_1 - S_0 gap same well reproduced at all hopping and Franck-Condon regions
- TD S_0 and S_1 populations match *ab-initio* ones
- S_1 to S_0 hopping starts at same time (55 fs)
- Similar distribution of hopping points

