On the Search for Minumum-Energy Conical Intersections in Mycosporine-like Amino Acids

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Overview

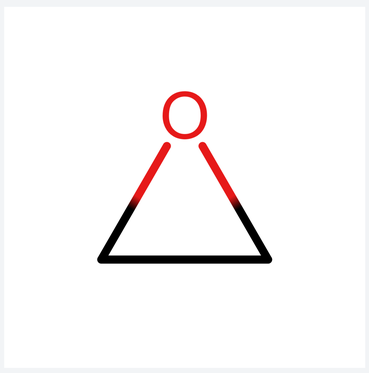
- Photochemistry governed by ultrafast non-radiative processes at conical intersections (CIs) of potential energy surfaces (PES).
- High computational cost associated with CI searches.
- Machine-learned interatiomic potentials (MLIPs) provide a mechanism for reducing computational cost of minimum-energy CI searches.

Mycosporine-like Amino Acids

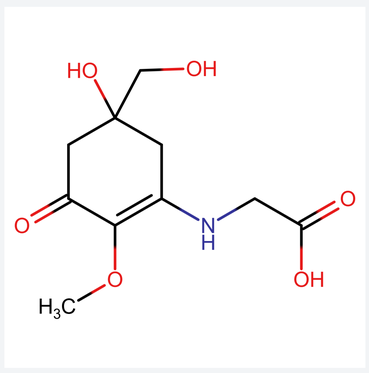
- Family of molecules centred on either a cyclohexenone or cyclohexenimine ring [1].
- Strong absorbance bands in both the UV-A ($315-400$nm) and UV-B ($280-315$nm) regions [1].
- High photostability with potential applications for UV protection [1].
- Differing non-radiative de-excitation pathways between cyclohexenones and cyclohexenimines.
- Primary interest in cyclohexenimines.

Molecular Targets

- Oxirane acts as a simple test case for the MECI search algorithm.
- Photoinduced Oxirane ring opening previously investigated [2].
- Previously identified S_0/S_1 CI in Oxirane [2].
- Mycosporine-Glycine (Myc-Gly) selected for its photorelevant S_0/S_1 CI.
- Myc-Gly has a lower dimensionality seam space compared to other MAAs, reducing search algorithm runtime.



(a) Oxirane



(b) Myc-Gly

Future Work

- Investigate molecular dependence of parameters in MECI search algorithm.
- Introduce a modified active learning loop to generates additional training data in extrapolative regions.
- Impose σ control logic and geometry constraints to fully automate the MECI search.
- Use more computationally-intensive ab initio methods like multistate spin-flip DFT in vicinity of CI candidates [3].
- Develop a generalised MACE model across a range of photosensitive organic molecules akin to MACE-OFF [4].

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MACE Model

- Higher order $E(3)$ equivariant message-passing neural network (MPNN) [5].
- Capable of generating force-fields and machine-learned interatomic potentials [5].
- Approximate potential energy surfaces (PESs) of molecules for constrained CI search.
- Form a 5-calculator ensemble and train on each state via ESTEEM package.
- Training loss given by weighted sum of mean square errors of energy, force components and dipole moments

MECI Search Algorithm

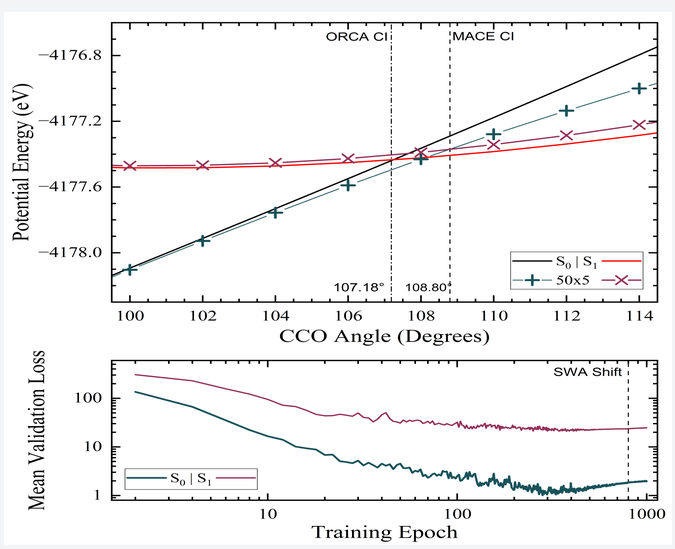
- New optimisation method analogous to the Yarkony approach [6] applied.
- Define an objective function for minimisation, (1), for two states I and $J = I + 1$ [7].
- Set $\sigma \in \mathbb{R}_{\geq 0}$ arbitrary and $\alpha = 0.54$eV.
- Minimise $\Delta E_{IJ}(\mathbf{r})$ with respect to $\mathbf{r}$ subject to constraints via a Powell optimisation scheme, varying σ monotonically.
- Ensure tractability by fixing a minimum optimisation threshold, $\delta = 0.027$eV [7].

$$F_{IJ}(\mathbf{r};\sigma,\alpha) = \frac{E_I(\mathbf{r}) + E_J(\mathbf{r})}{2} + \sigma\frac{\Delta E_{IJ}^2}{\Delta E_{IJ} + \alpha} \tag{1}$$

$$\Delta E_{IJ}(\mathbf{r}) = E_I(\mathbf{r}) - E_J(\mathbf{r}) \tag{2}$$

MECI Search on Oxirane

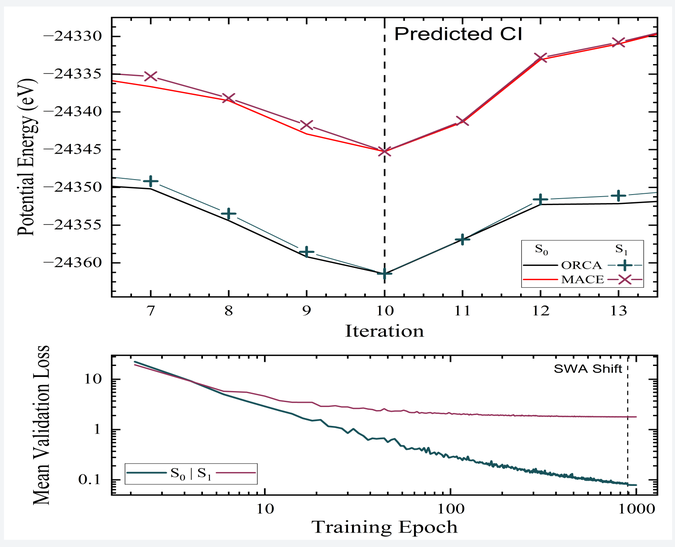
- Training data generated by rattling an optimised oxirane conformer in vacuuo.
- (TD-)DFT calculations performed for sets of 50 rattled molecular configurations for each state.
- Validation-Training partition of $5\% - 95\%$.
- Ten additional rattled configurations for every 10-degree interval between 70 and 110 degrees.
- Models trained for 1000 epochs with a stochastic weight averaging (SWA) shift applied at epoch 800.



- MACE CI at 107.18° compared to TD-DFT CI at 108.80°.
- Good agreement with the observed S_0/S_1 CI in other work [2].
- MACE converges to TD-DFT result over successive training iterations.
- Mean model adoption at epoch 472.6 and 222 for S_0 and S_1 states respectively.
- Early adoption indicative of high training rate.
- Absolute forces in excess of 2.5eV/Å raises issues with rattled data.

MECI Search on Mycosporine-Glycine

- 300 item datasets generated via 125fs stochastic Langevin MD simulations with pseudorandom sampled temperatures.
- Optimised in-vacuuo Myc-Gly conformer used with MACE-OFF organic force field for initial configurations [4].
- Validation-Training partition of $17\% - 83\%$.
- MACE models trained for 1000 epochs with a SWA shift applied at epoch 900.



- Previously unidentified CI candidate.
- MACE energy gap of 1.02×10^{-2} eV and TD-DFT energy gap of 2.6×10^{-2} eV at CI candidate.
- Energy divergence of 16.17 eV and 16.20 eV for the S_0 and S_1 states respectively.
- Mean model adoption at epoch 893.2 and 831 for S_0 and S_1 states respectively.
- No indication of the photorelevant S_0/S_1 CI at level of TD-DFT theory used.

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