Classical dynamics on a neural network - interpolated potential energy surface

The problem of simulating the dynamics of a molecular system can be treated in a number of ways. It is in principle a quantum mechanical problem where the time-dependent Schrödinger's equation must be solved, this is however a prohibitively expensive approach. Among other options, classical mechanics simulations can be a good approximation in some cases while being much cheaper and easier to implement.

Several assumptions are made when treating a quantum system classically, but the main idea is to consider hard objects subjected to some external potential; this potential in itself is dependent on the positions of the objects and is what is called a potential energy surface (PES). Once the PES has been set-up, the simulation reduces to solving Newton's equation using some integration algorithm.

The PES used for small molecules usually comes from electronic structure (ES) calculations using theories such as Hartree-Fock and DFT, however these methods are often expensive (depending on the basis set) having in mind the number of energy and gradient calculations necessary for this kind of simulation.

Problem

As these ES calculations are too expensive, it is necessary to find another approach for energy and gradient evaluations. This may consist of a much cheaper interpolation on a number of points calculated with the ES methods, which can be in fact done using a neural network (NN).

Consequently, in this work the construction of a PES by interpolation with a NN is attempted.

Methods

The molecule we'll be simulating is $HCOH^+$, an open shell cation. For the sampling of the initial configurations for the training data, some structures are used as recovered from [1] (actually I had these structures at hand because the author is my thesis supervisor, however none of this had been previously done by us). The lowest energy critical points were selected and new examples were generated by adding random noise to the interatomic distances. The energies of these configurations were calculated with the ES package Psi4 [2] at the level UHF/cc-pVDZ. In total 1000 data points were generated but this dataset was further expanded by exploiting the permutational symmetry of the molecule, that is, swapping identical atoms, in this case the hydrogens, leading to a total of 2000 data points.

The interpolation was performed using a NN with 4 hidden layers that takes as input a vector containing all the inverse distances between each pair of atoms, and whose output are the energies in Hartree. These hidden layers contained, respectively, 512, 254, 128 and 128 neurons, which was selected since gave the best and most reproducible results.

Once the PES was constructed, the gradients with respect to the coordinates of the atoms (proportional to the forces) were calculated using TensorFlow. Subsequently, the trajectories were run on this using the Velocity-Verlet integration algorithm, which gives position, velocity and acceleration at the same time t, as opposed to others such as leapfrog or Verlet algorithms.

Results

Using the aforementioned data set, the NN was trained for 500 epochs, which gave a training loss (MAE) of 0.0010, and a validation loss of 0.0027 (Hartree). It is noteworthy that a training error of about 5.0 kJ/mol (~0.0019 Hartree) was obtained in [1] while using other method involving energies, gradients and hessian matrices for the interpolation, so these results are somehow promising.

The NN-PES was tested on a representative slice, while comparing to the true PES (HF), figure 1 shows the results of this.
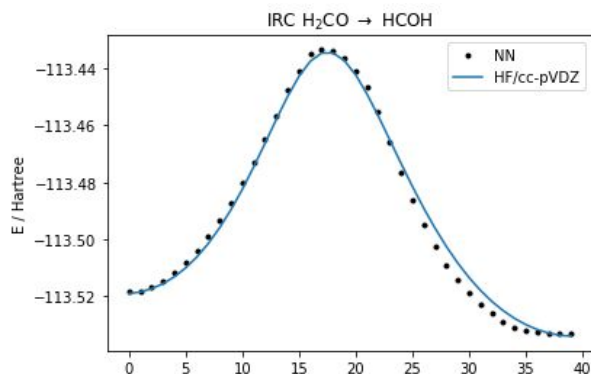
From this plot it can be seen that the topology is somehow preserved for much of the points, however at some points it is distorted, which may be due to the lack of gradient information inputted to the NN.

Figure 1. Comparison of a slice of the PES: NN vs HF.

As the final (and main) results are the classical mechanical trajectories of the molecules. Some trajectories were run using parameters extracted from [1] so as to try to reproduce the results there. Most of these trajectories didn't make much sense since the molecule usually ended up falling apart even when they were close to a supposedly low energy structure. These results may be due in part to some lack of sampling since very high energy structures weren't sampled at all, which in turn leads to the NN not knowing that two atoms can't be too close, among other things.

A trajectory was run using HF gradients (which took about 30 min), and using the NN (11 s) under the exact same initial conditions, which of course lead to very weird results for the NN while the HF trajectory gave very consistent results (what is expected at least), discarding significant errors on the integration algorithm.

Conclusions

This work shows that, although a NN is capable of fitting a number of data points (coordinates, energy), the results might not be accurate enough for performing classical dynamics simulations. In addition, better sampling techniques are needed for the NN surface to be any useful.

Future additions to the code may include the enhancement of the PES by adding some of the points on the simulated trajectories, as well as adding the gradients as a new input for the NN, so the topology is better described.

References

[1] Gloria E Moyano, Seth A Jones and Michael A Collins. J Chem. Phys. 124, 12, 124-318 (2006). https://aip.scitation.org/doi/10.1063/1.2181571

[2] The Psi4 project. http://www.psicode.org/