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Cybertraining Workshop Project Writeup

Parameter Fitting with FOX:

My first small project consisted of optimizing Lennard Jones parameters for a $Cd_{44}S_{44}$ quantum dot. I originally computed a ~500fs trajectory for the node of a metal-organic framework, as obtaining MOF parameters was the original goal, however CP2K MM is required and seems to have some issues with cerium, so maybe MM for lanthanides is not straightforward. The longer-term goal for using this software is to obtain good LJ parameters for a decent range of MOF nodes (as good parameters exist already for most organic molecules in the ligands) for usage in a particle swarm optimizer I have to determine globally optimal binding sites of small molecules.

With the issue associated with cerium atoms, I didn't have time to run another full QM trajectory, so I took 500fs of an AIMD trajectory that was used in a quantum dot project. From there I just specified charge constraints, and used UFF parameters as the input. I also looked into usage of the guess_rdf.py script based off of the QM trajectory, but it seemed that I was getting negative epsilons, so I just went with UFF for the initial guess.

Results:

I ran a little over 600 MD simulations in order to optimize the parameters, at which point I took the best iteration which was the 413th trajectory. Errors are plotted below in Figure 1, and Figure 2 contains the comparisons between the RDFs between the best MM trajectory and the QM trajectory.

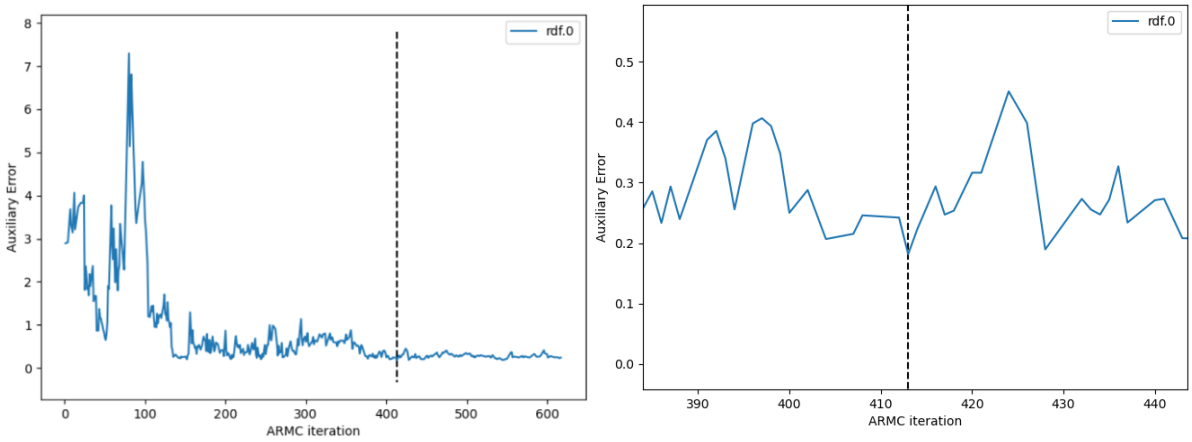

Figure 1 Full error tracking in the parameter optimization (Left). Error zoomed in around the best iteration (Right).

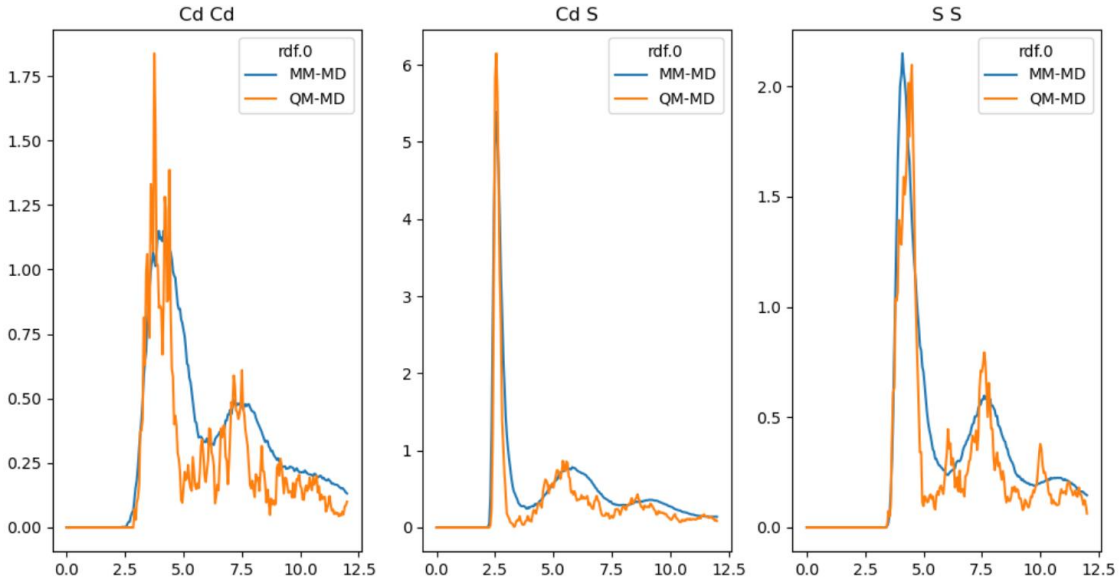

Figure 2 RDF for the three bond types in the $Cd_{44}S_{44}$ quantum dot, with the QM trajectory in orange, and MM in blue.

NAC Computations with with CP2K/Libra:

Another small project I worked on was familiarizing myself with the computation of NACs using CP2K/Libra. This was a goal due to the fact that computations of NACs in Quantum Espresso has been quite slow. The real goal is to do this for a few variations of a ligated quantum dot, however being that the system ranges from 88-125 atoms, this was not going to be feasible within the workshop. With that being the case, I chose a simple imidazole ring to run a short trajectory for. I've had a number of issues with this process, first due to selection of the wrong orbitals for computation of the NACs. This was fixed, and a new geometry was run, however there is likely some sort of issue with either the trajectory or cutoffs for the system. Some of the time steps are missing data in the res/ folder which appears to be due to unconverged calculations. There are also time steps for which the overlap matrix is not invertible. Beyond that, the vibronic Hamiltonian in the KS basis is completely diagonal, so there is definitely some sort of issue which I was not able to figure out by the time this workshop ended. I think I will likely swap to computation of the NACs using VASP or something also, as the real hope was that CP2K would be significantly faster, but this did not really prove to be the case from the tests I ran on the full ligated quantum dot.

1D MIW Implementation:

What I spent the bulk of my time on was working on an implementation of the MIW approach to modelling quantum phenomena (Hall, M. J. W. *Phys. Rev. X* **2014**). The longer-term goal associated with this project is to implement the fully generalized formulation of the approach, together with efficient classical MD computations being carried out within each world (Sturniolo, S. *Phys. Rev. E* **2018**). I did not want to rush the implementation of the full approach, so here I simply have a 1D implementation. The code for this was definitely rushed to meet the end of the workshop, so it is quite poorly commented/structured. However some nice results were able to be obtained, such as the tendency towards recreation of a gaussian wavefunction for the ground state of the quantum harmonic oscillator in Figure 3. The 'ground state' is obtained through a pretty straightforward minimization algorithm which amounts to really just being a sort of damped MD simulation. The difficulties associated with this project were not really due to the complexity of the implementation, just due to the extreme numerical instabilities that arise from the forces. Nearly every pairwise interaction between the worlds comes in the form of something proportional to some power of inverse of the distance between the world particles. This meant that tuning the number of worlds, spacing of the worlds, interaction strength, and relative strength of the MIW potential compared with that of the classical harmonic potential was really quite a nightmare. An adaptive step size had to be used within a Verlet integrator, scaling down based off of a step rejection criteria satisfying the proper ordering of the worlds. This clearly came at the cost of the conservation of energy, so a lot of work still needs to be done. The implementation of the full approach detailed by Sturniolo is more complicated, but should be much less sensitive to these issues.

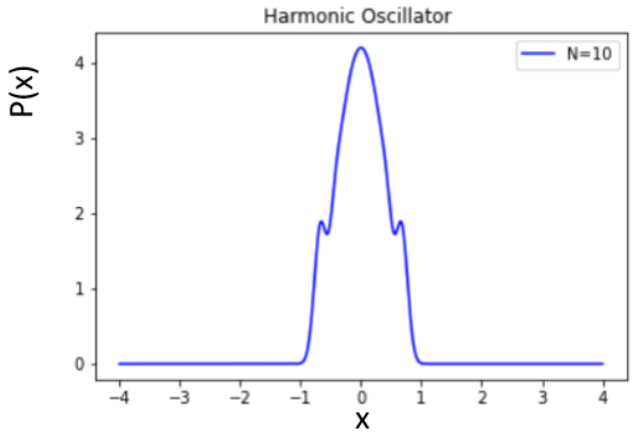

Figure 3 P(x) constructed by summing gaussians centered on the minimized coordinates of the 10 worlds. Suggestion is that P(x) can have an interpretation similar to |\Psi(x)|^2 under certain circumstances.

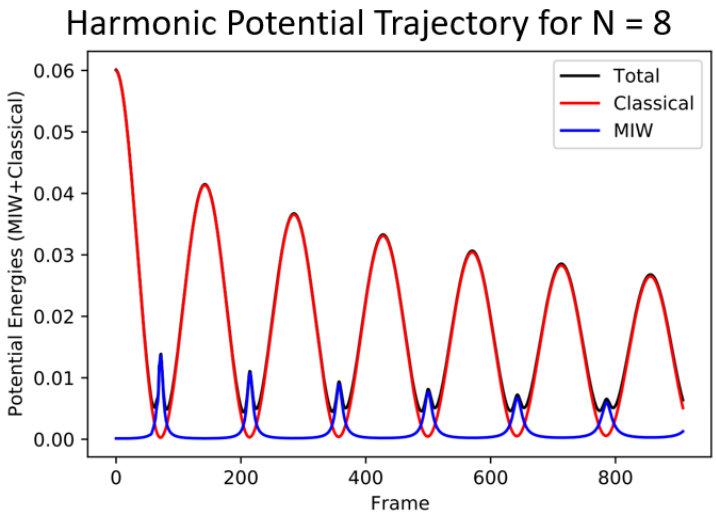

Figure 4 Energies plotted through the harmonic potential trajectories.

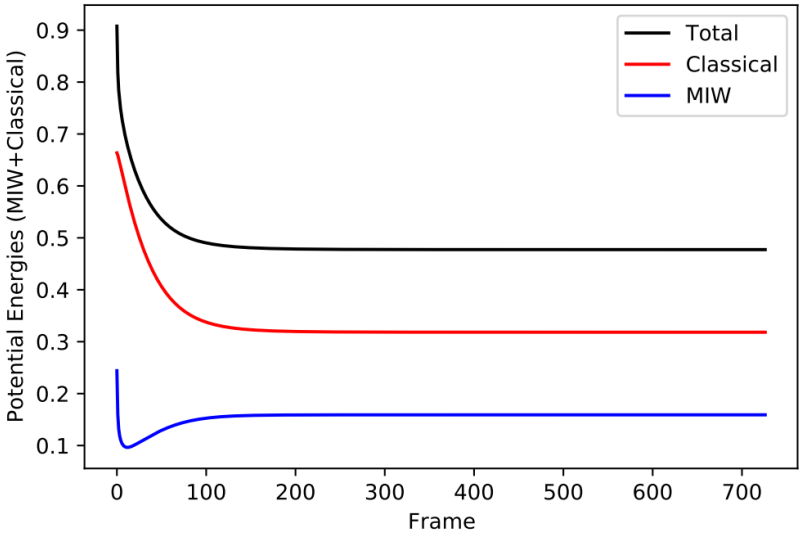

Figure 5 Example of energies tracked through an MD-minimization scheme.