

Abstract

An empirical Molecular Dynamics (MD) force-field's usefulness is limited by the suitability of its parameter set. FFOpt is a general approach for optimization of these parameters. The method the high dimensional parameter space, searching for error minima. The error is determined by comparison of MD data with external data. These data can consist of experimentally determined quantities as well as the results of *ab initio* quantum calculations. Different geometries are used to generate comparable data in MD as well as quantum methods. The method has been applied to the PuReMD reactive MD software package. A training set of quantum mechanical data was used to tune a force-field for the simulation of water systems. We present the results of the parameter fitting procedure, as well as comparison of PuReMD using refined potentials with experimental and conventional MD data.

Training Set Generation

Geometries for training sets are automatically generated and fall into three categories:

- Three-body: for each triplet of atom types, bond angles and lengths are varied.
- Four-body: torsion angle is rotated about energy minimum
- Random: generated at various stoichiometric ratios

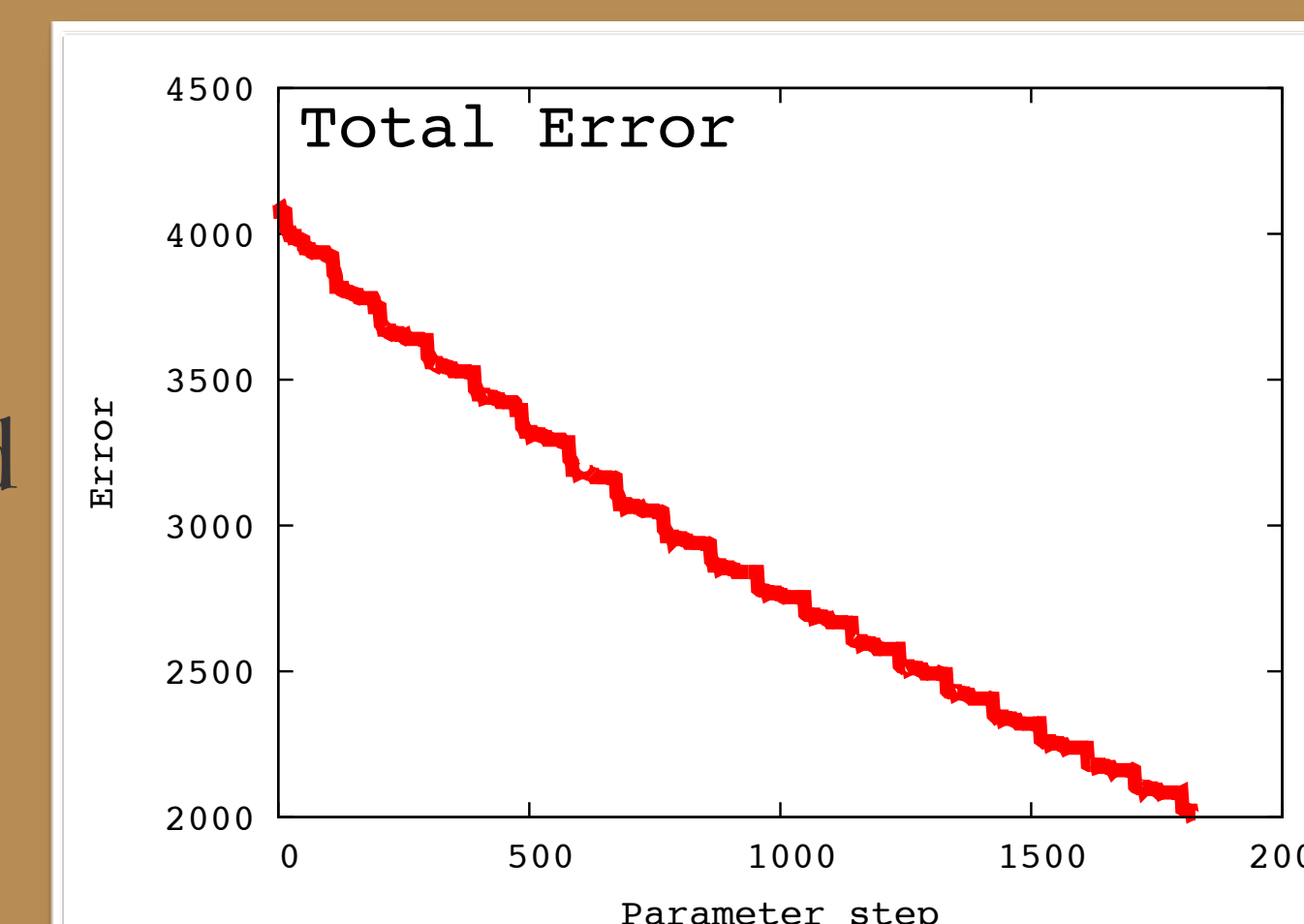
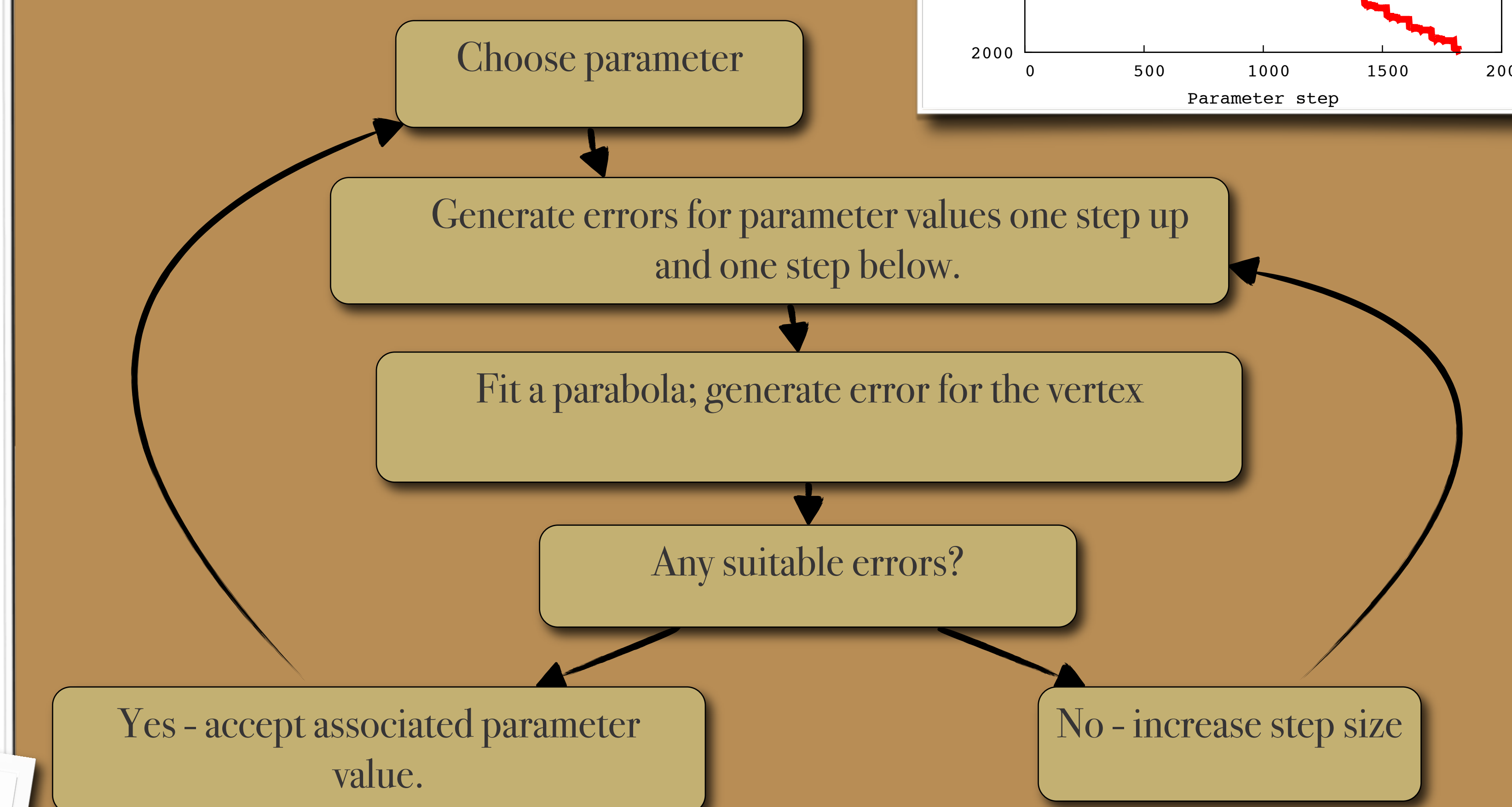
Smaller systems were included to fit energies far from equilibrium configurations, whereas the larger random systems were used to match equilibrium data. Quantum *ab initio* calculations were performed using Gaussian (V09, Revision B.01). Three-body single point calculations were performed using B3LYP with a 6-311g basis set with diffuse and polarization functions. Four-body geometry optimizations and single point energy calculations were performed using a coupled cluster method and a correlation consistent basis set. Random systems were optimized using multiple steps of increasing accuracy. Systems were first optimized with a semi-empirical method using the PM6 Hamiltonian followed by two B3LYP

calculations, one with the 6-311g basis set and one adding diffuse and polarization functions. Single point energies were considered for three and four body systems, while random systems also included Mulliken partial charges and Wiberg bond index for comparison.

Systems were constructed consisting of oxygen and hydrogen. For four-body systems, only hydrogen peroxide (HOOH) was considered. In total, 3781 three- and four-body systems were constructed. Random systems were generated with O-H ratios of 1-1, 1-2, 1-0 and 0-1 for a total of 27 systems.

Force Field Optimization

Parameters for PuReMD were optimized individually in an iterative procedure:

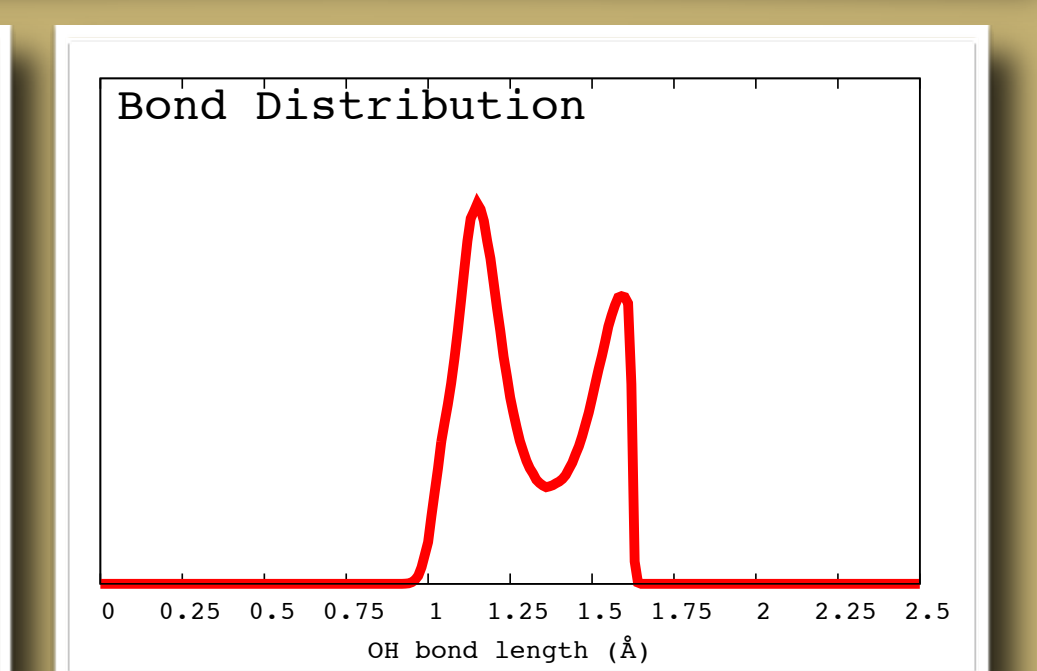
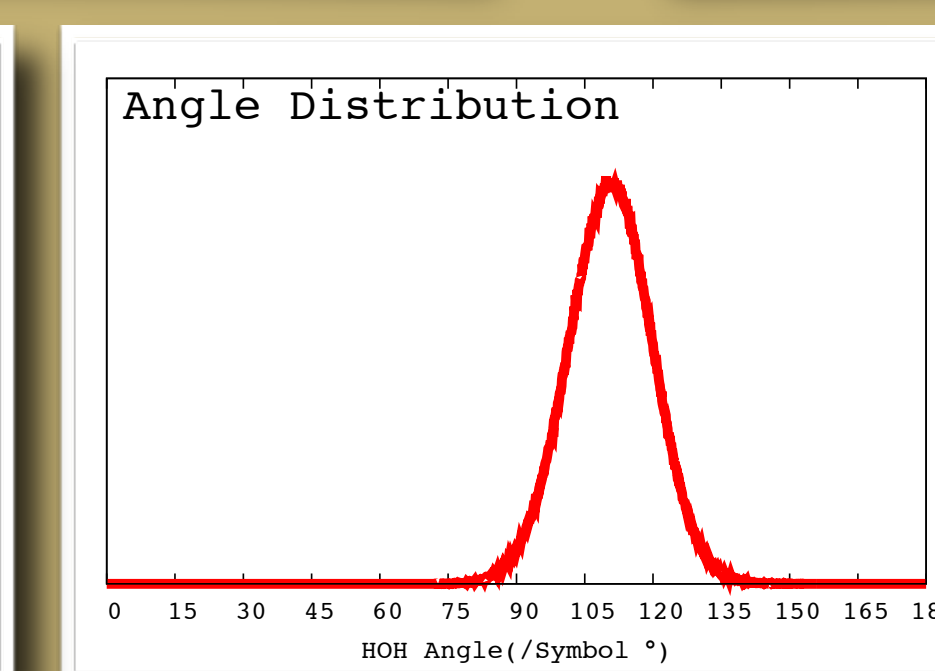
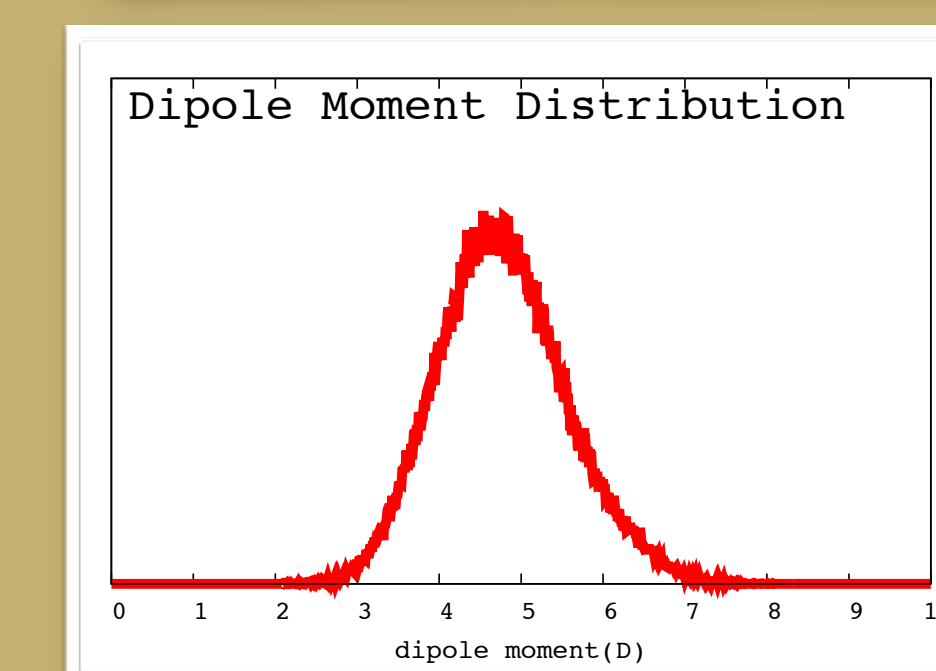
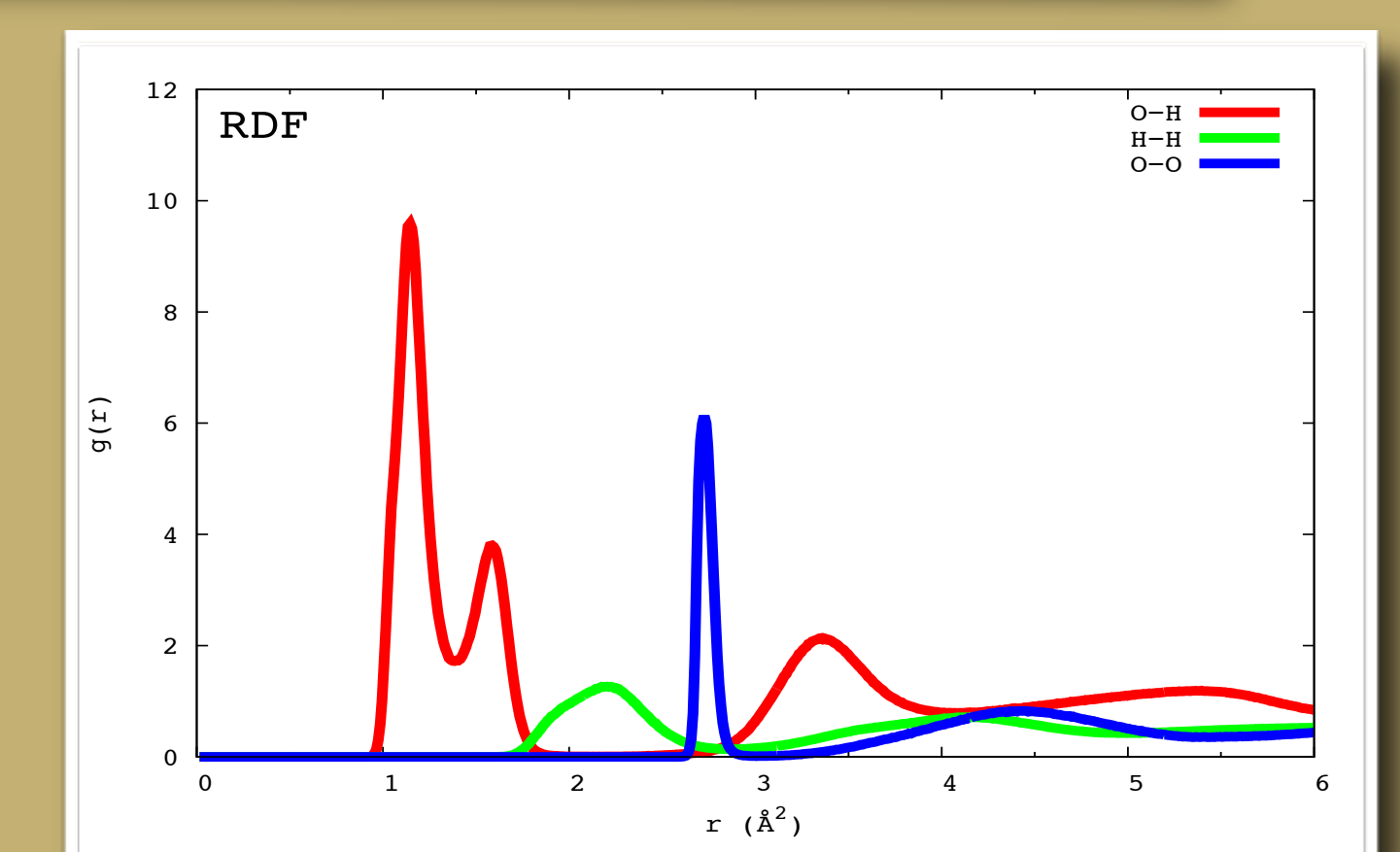
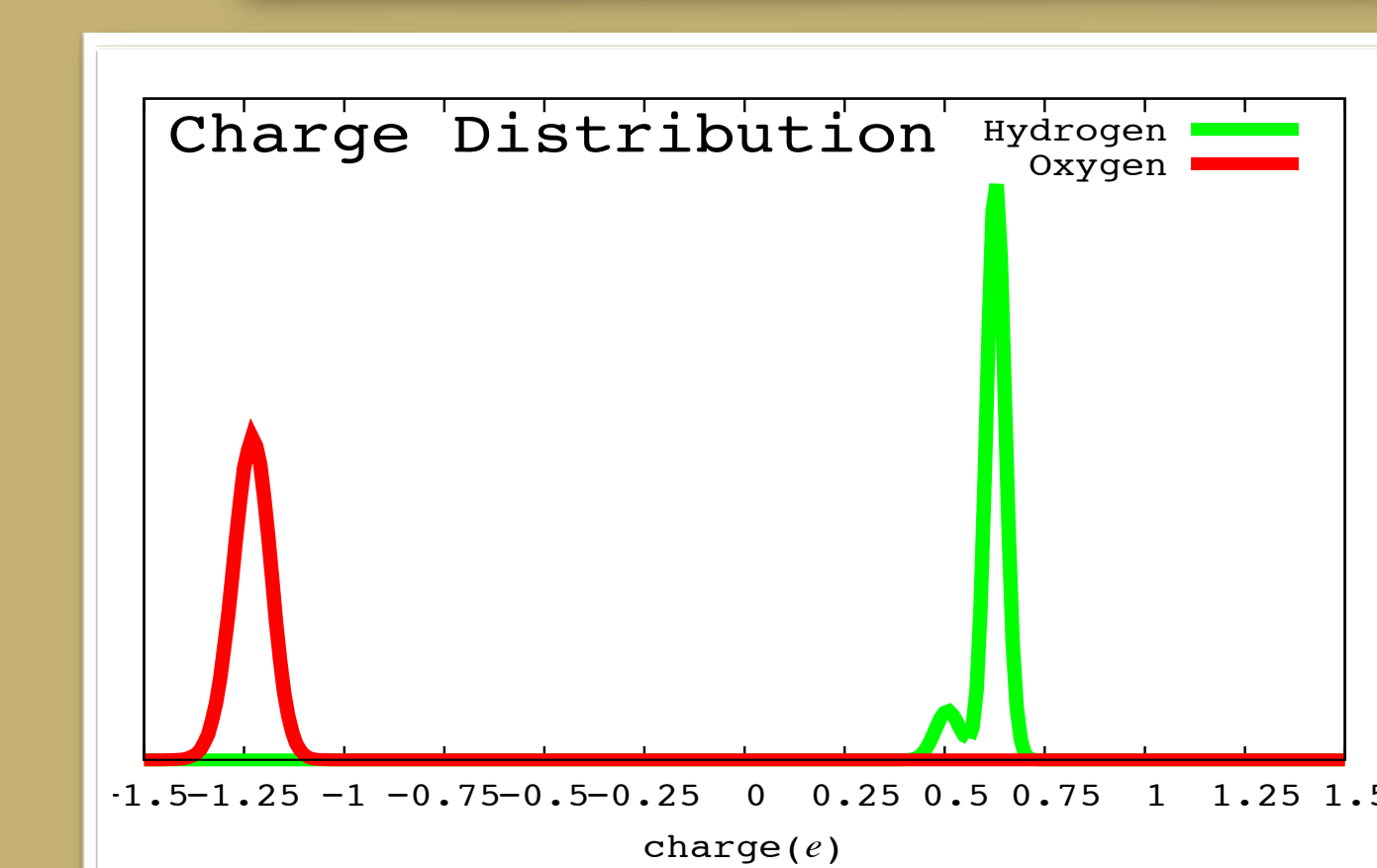
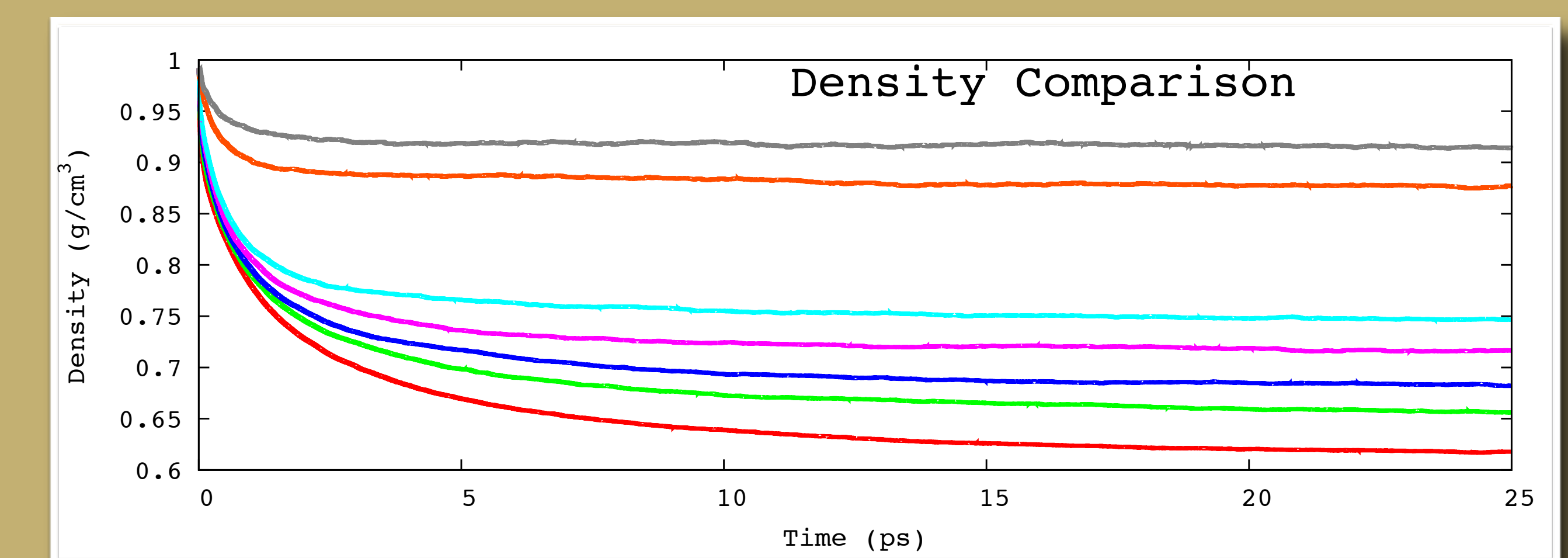


Results

For each parameter set, a water system consisting of 2025 waters at 1 atm and 300K in an isothermal isobaric ensemble with Nosé-Hoover thermostat and a

Berendsen barostat was simulated using Reactive MD. Several macroscopic observables were calculated.

Observable	Reax Data	SPC	Experimental
O-H Bond (Å)	1.152	1.00	0.957
H-O-H Angle (°)	110.6	109.47	104.5
O Charge (e)	-1.230	-0.8476	-
H Charge (e)	0.615	0.4238	-
Dipole Moment (D)	4.78	2.424	2.9
Density(g/cm ³)	0.917	0.981	0.997



Conclusions

- As optimization continues, total error with respect to the quantum data set continues to be reduced.
- As error is decreased, computed observables from trial simulations exhibit a trend toward expected values.
- Once error has reached a low enough level, observables are expected to match more accurately.