

The Principal Hugoniot of Deuterium: Potential Pitfalls of Beyond-DFT Thermodynamic Sampling

Raymond Clay¹

¹Sandia National Laboratories, Albuquerque, New Mexico 87123

Density functional theory is the workhorse of *ab initio* equation of state calculations at extreme conditions due to its reasonable computational cost and significantly improved accuracy over chemical models. However, the often unquantified errors arising from the choice of exchange-correlation functional make thermodynamic sampling based on many-body methods appealing. One proposed beyond-DFT method is “coupled electron-ion Monte Carlo” (CEIMC), which explicitly treats many-body electronic exchange and correlation effects with ground state projector Monte Carlo. Troublingly, the principal Hugoniot of deuterium calculated with CEIMC deviates significantly from density functional theory calculations and experiment. In particular, CEIMC predicts too soft of a Hugoniot, which both fails to match well established gas gun data and predicts a peak compression roughly 7% larger than experiment. In this talk, we attempt to isolate the source of this discrepancy. Starting from a perturbative expansion of the Rankine-Hugoniot relations in energy and pressure errors, we will quantify errors peculiar to CEIMC and look at their impacts on the calculated Hugoniot. While this talk focuses mostly on CEIMC, much of the concerns are general to thermodynamic sampling based on many-body methods.

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