The Deuterium Hugoniot: Pitfalls of Beyond-DFT Thermodynamic Sampling

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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 both density functional theory calculations and experiments [1]. 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 [2]. In this talk, we demonstrate that in the absence of all other sources of error, the commonly employed fixed-node approximation in projector QMC can introduce energy and pressure errors large enough to account for the discrepancy between the CEIMC Hugoniot and experiment. We demonstrate this by deriving a first-order equation for the dependence of the density of a predicted Hugoniot point on energy, pressure, and volume errors. Using configuration interaction type wave functions with projector QMC in small simulation cells, we estimate the size of the fixed-node error for the class of wave functions used in CEIMC at pressure and temperature conditions relevant for the principal Hugoniot. These estimated errors in conjunction with our formula for the first-order density change allow us to account for the vast majority of the discrepancy between CEIMC and experiments [1]. In contrast, we find that several functionals that achieve excellent agreement with experiment do so through error cancellation, which we contend accounts for their observed poor performance in predicting the reshock measurements [2]. While this talk focuses primarily on CEIMC, most of the issues discussed are general to all wave function based methods for treating the electronic structure.

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REFERENCES

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