Quantum Monte Carlo Benchmarks of Density Functional Theory: High Pressure Materials and Liquid Water

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We use highly accurate quantum Monte Carlo calculations to benchmark the accuracy of typically employed approximations to the exchange-correlation functional in density functional theory. We study 2 systems where density functional theory has found limited success: metal-insulator transitions in light elements at high pressure and liquid water. In both cases, we present a detailed analysis of many of the functionals typically used in the study of solids and we correlate the accuracy of the functional with the details of its construction. In the case of hydrogen and hydrogen-helium mixtures at high pressure, the location of dissociation and metallization transitions in both liquid and solid phases is found to be very sensitive to the exchange-correlation functional. In the case of liquid water, both short-range exchange repulsion and dispersion interactions are shown to play a crucial role in the accurate description of the liquid. This work was performed under the auspices of the US DOE by LLNL under Contract DE-AC52-07NA27344. The work was supported through the Predictive Theory and Modeling for Materials and Chemical Science program by the U.S. Department of Energy Office of Science, Basic Energy Sciences (BES).