Characterization of the liquid–liquid phase transition in dense hydrogen: The role of accurate exchange-correlation and nuclear quantum effects

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The properties of dense liquid hydrogen, the most abundant form of matter in our solar system, play an essential role in planetary science and fusion research. Its liquid–liquid phase transition (LLPT) is associated with the dissociation of molecular hydrogen resulting in an insulator-to-metal transition (IMT). Recently, the pressure–temperature boundary of the IMT was predicted by means of *ab-initio* molecular dynamics (AIMD) simulations within the density functional theory framework with use of the most-advanced meta-GGA level exchange-correlation (XC) functional, SCAN/SCAN-L, with the long-range van-der Waals interaction correction rVV10 [J. Hinz *et al.*, "Examining the insulator-to-metal transition in warm dense hydrogen by density functional theory with advanced exchange-correlation functionals," to be submitted to Physical Review Letters]. Nuclear quantum effects were taken into account by means of path-integral molecular dynamics. Several studies have predicted the first-order nature of this transition at high pressure; however, the IMT boundary line in the phase diagram and determination of its critical point position strongly depend on the theoretical methods. In this work we show that the use of the standard GGA-level PBE XC functional together with the classical treatment of ions leads to a partial error cancellation, therefore providing reasonable results in some range of pressures. For accurate characterization of the LLPT without relying on the error cancelation, we perform AIMD with the accurate SCAN+rVV10 XC functional and quantum treatment of ions within the isothermal-isobaric (*NPT*) ensemble, the most useful statistical ensemble for systems near or across first-order transitions. Density jumps are observed across the LLPT and an accurate estimate for the critical point location is provided.

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