Diffusion Monte Carlo Study of High-Pressure Solid Hydrogen Phases

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The high-pressure phase diagram of hydrogen has garnered much research interest ever since it came to light that hydrogen might transition into a metallic state at high pressure. Nowadays, the relevance of studying hydrogen under high pressure also comes from astrophysics as hydrogen is the largest constituent of most of the stars and gaseous planets, and is subject to extreme pressure and temperature in the interior of those celestial objects.

Hydrogen is believed to transform into its atomic metallic phase with a crystal structure belonging to the $I4_1/amd$ space group (also often called *Cs*-IV structure) at around 500 GPa. Said pressure is already near the limit of what is currently achievable by the experimental apparatus such as the diamond anvil cells. Consequently, one has to rely on computational methods for investigating the hydrogen phase diagram in the pressure regime beyond 500 GPa.

Previous computational studies employing a crystal structure search together with the density functional theory (DFT) method predicted that *Cs*-IV phase is stable up to 2000 GPa. Their structure search also uncovered some novel structures such as the *oC*12 and *cI*16 structures that are predicted to become more stable than *Cs*-IV above 2000 GPa.

In this thesis, the phase diagram of high-pressure solid hydrogen is investigated within the pressure range of 500 GPa to 2000 GPa. The diffusion quantum Monte Carlo (QMC) method is employed to evaluate the static enthalpy of candidate structures, while their zero-point energy is calculated via harmonic approximation from DFT forces. DMC is known to be more reliable in its treatment of electronic structure than DFT, at the cost of being more computationally heavy. Additionally, an evolutionary crystal structure search is employed to obtain more candidate structures that are energetically competitive.

This study revealed that the *Pnma* structure discovered by the previous study is already more stable than *Cs*-IV at 2000 GPa. Two of the new candidate structures discovered in this work managed to become more stable than *Cs*-IV at some point within 500 GPa to 2000 GPa. The inclusion of the aforementioned structures modified the phase diagram of solid hydrogen in said pressure range. Hydrogen is predicted to undergo phase transitions in the order of *Cs*-IV → *C2/c*-6 → *Cs*-IV → *C2/c*-10 → *Pnma*, where the transitions happen at 800 GPa, 900 GPa, 1000 GPa, and 2000 GPa.