The binding of atomic hydrogen on graphene from density functional theory and diffusion Monte Carlo calculations

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The binding of hydrogen on graphene is relevant to the use of graphene and graphitic surfaces for hydrogen storage and other industrial applications. However, a reliable theoretical description of interactions at the graphene surface has proven to be challenging for density functional theory (DFT). Instead, a reliable description can be obtained through treating the system with diffusion Monte Carlo (DMC). DMC is a real-space stochastic approach to solving the many-body Schrödinger equation which is particularly attractive given its low scaling with the number of electrons and its high parallelizability. In this work DFT and DMC methods are used to calculate the binding energy of a H atom chemisorbed on the graphene surface. The DMC value of the binding energy is about 16% smaller in magnitude than the Perdew-Burke-Ernzerhof (PBE) result. The inclusion of exact exchange through the use of the Heyd–Scuseria–Ernzerhof (HSE) functional brings the DFT value of the binding energy closer in line with the DMC result. It is also found that there are significant differences in the charge distributions determined using PBE and DMC approaches.