Molecular hydrogen adsorbed on benzene: insights from a quantum Monte Carlo study[1]

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We present a quantum Monte Carlo study of the hydrogen-benzene system where binding is very weak. We demonstrate that the binding is well described at both variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) levels by a Jastrow correlated single determinant geminal wave function with an optimized compact basis set that includes diffuse orbitals.[2] Agreement between VMC and fixed-node DMC binding energies is found to be within 0.18 mHa, suggesting the calculations are well-converged with respect to the basis. Essentially the same binding is also found in independent DMC calculations using a different trial wave function of a more conventional Slater-Jastrow form, supporting our conclusion that the binding energy is accurate and includes all effects of correlation. We compare with empirical models[3] and previous calculations,[4] and we discuss the physical mechanisms of the interaction, the role of diffuse basis functions, and the charge redistribution in the bond.

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