

Title	水素貯蔵材料における分子吸着相互作用の第一原理解析
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# Abstract

Hydrogen is an interesting candidate for an environmentally-friendly energy carrier, due to its low weight, ability to be produced from water through electrolysis, and carbon-less combustion by-product. Storing hydrogen however, is known to be notoriously difficult, requiring very high pressure or ultra low temperature to satisfy certain industrial requirements. This remains one of the most important bottleneck to its more widespread adoption.

In a separate development, nanotechnologies have enabled high performance materials beyond what is conventionally possible. Relevant to the problem is the development of nanostructures allowing increased surface area and optimized shape, with examples such as carbon nanotubes (CNTs) and silicon carbide nanotubes (SiCNTs). To further enhance their performance, surface modifications by doping or defect formation is being continuously investigated, although the sheer amount of possible combination of materials and structures means experimental researches have seen limited progress.

Material informatics is a promising emerging field, offering faster iteration at lowered cost. With the help of massive computational facilities and multiscale modelling, from fundamental *ab initio* physics to coarse grained models with observable physical quantities, material properties can be estimated without the need for expensive experimentation. Unfortunately, the hydrogen interaction with the nanostructures is dominated by van der Waals (vdW) force, which has its origin in quantum fluctuation thus causing the popular density functional theory (DFT) to fail. Ideas for incorporating vdW into DFT have been explored in recent years, however these corrections can fail in different manner for different materials, making it difficult to judge their accuracy. If reference experimental data are widely available, it becomes a simple problem of finding which one best matches the reference, however this severely limits the reach of material informatics in handling novel materials.

Quantum Monte Carlo (QMC), in particular the diffusion Monte Carlo (DMC) is a separate approach that completely avoids the problem by solving the true many body wavefunction, therefore treating vdW by default without any corrections. In the past, its application is limited to small systems due to the lack of computational power, but with the development of supercomputers it is increasingly applied to larger problems. Moreover, the algorithm is fundamentally more amenable to parallelization than the conventional DFT, allowing it to run at a higher scale. Its accuracy means that it can be used for generating reference values in lieu of experimentation, accelerating the search for hydrogen storage material while also helping the development of the vdW corrections into DFT.

The present work demonstrates the utility and benefit of having DMC as a reliable benchmark, using the H<sub>2</sub> on SiCNT as the model system. SiCNT is one of the more promising candidate materials, having suitable bond length with better adsorbance than CNT. It is also often used for benchmark given the variability of its binding energy with regard to the chosen exchange-correlation functional. The plain local density approximation and generalized gradient model was found to (predictably) be insufficient, with significant over-/under-estimation of the binding energy and inaccurate geometry. Tkatchenko-Scheffler pairwise correction and vdW-DF2 nonlocal functional were found to best approximate DMC energetics, within 0.25 kcal/mol of the predicted 1.370(106) kcal/mol binding energy, while the geometry were found to be best predicted by exchange-dipole model and DFT+D3. Charge density analysis revealed some nonlocal functionals to produce unphysical densities, but with seemingly no bearing on the optimized geometry. It is concluded that combinations of corrections should be used at different stages (geometry and energy) for the most accurate result.

**Keywords:** Hydrogen storage, SiCNT, van der Waals, *ab initio*, Diffusion Monte Carlo