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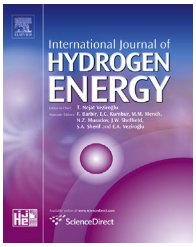

Comparative studies of adsorption capacities for graphene based sorbents with different potential functions in molecular simulations

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ABSTRACT

The reliabilities of $C-H_2$ interaction potential functions are of great importance in the molecular simulation for accurate predictions of carbon-based hydrogen storage materials. In this work, by implementing the DFT–vdW calculations, we propose an *exp-8* form $C-H_2$ potential function and compared with three widely used functions for the hydrogen molecules adsorbed onto graphene. Studies show that the simulated results by using the *exp-8* potential function are in good agreement with experiments at 298 K, while other three potential functions are not enough to describe the $C-H_2$ interactions due to the mismatch of the stable adsorption distance and the interaction strength. At 77 K, all four potentials give overestimated predictions compared with experimental investigations. We suggest that the adsorption sites and hydrogen molecule orientations should be considered when constructing the $C-H_2$ potential function since they have large influences on the interactions between hydrogen molecules and graphene sorbents. With such modified potential functions, the computation precisions are expected to be improved and a relatively accurate prediction for the storage capability of carbon-based hydrogen storage materials is becoming feasible.

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Introduction

Molecular simulations employing empirical potential energy functions are becoming increasingly important and prevalent, providing practical guidance on the experimental explorations in many research fields. A typical example is the simulation of hydrogen storage in carbon-based sorbents [1–3]. By using an empirical potential function to describe the complex interactions between hydrogen molecules and carbon sorbents in molecular simulations, it is now able to study large systems that cannot be handled with quantum calculations under current computational resources. Generally, the simulation accuracy is largely dependent on the selections of potential functions that describe the van der Waals interactions between hydrogen molecules and carbon materials [1,3,4] and hence, accurate potential functions for $C-H_2$ interactions with

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high computation efficiency are valuable for the theoretical research of carbon-based hydrogen sorbents materials.

Currently, two types of C–H_2 potential functions, the Lennard-Jones (LJ) [5–7] and the Buckingham potential functions [4,8,9], have been proposed for abovementioned goals. The LJ potential function $(U = A \bullet r^{-12} - B \bullet r^{-6},)$ (12-6 LJ form) is the most widely used one for the C–H_2 interactions with an r^{-12} term to describe the short-range repulsive force and an r^{-6} term for the long-range attractive part. Mathematically, LJ function is simple and convenient to be implemented, can well describe the non-bonded dispersive interactions. By using the LJ potential function with the parameters taken from different methods [10–12], the hydrogen storage capacities of various carbon materials (graphite [5,9], nanotubes [6,13], foams [4,14], etc.) have been evaluated to help better design new hydrogen sorbent materials.

Despite its wide usages, the 12-6 LJ form potential applied for the complex C–H_2 interactions is still not accurate enough. Usually, the hydrogen molecules are physisorbed onto sorbents via complex interactions (e.g. dispersive, electrostatic and orbital interactions etc.), it is questionable that the r^{-6} and r^{-12} terms in the LJ potential function are enough to describe the attractive and repulsive interactions, respectively. For the pure carbon sorbents, since there is little electron transfer and almost zero charge on the carbon atom, it seems that the attractive interaction between hydrogen molecules and carbon sorbents are almost the dispersive interaction that can be described by an r^{-6} term. However, reports show that the mathematically simple r^{-12} term in LJ potential function is too hard for the short-range repulsive interaction and may lead to huge calculation errors under large pressures [15].

Based on these considerations, the short-range r^{-12} term in LJ potential function is replaced by a soft $e^{-\alpha r}$ term, being called as the Buckingham potential function $(U = A \bullet \exp(-\alpha \bullet r) - B \bullet r^{-6})$ [16]. With this new function, Ihm et al. found that [17] the hydrogen storage capability for the expanded graphite agrees well with the experiments (3 wt% maximum uptake at 298 K and 20 MPa) when the interlayer separation distance is 9 Å [18]. Nevertheless, a strong Buckingham potential function can even give double of the hydrogen storage capacity of carbon foams than a weak LJ potential [4]. Such large differences in the simulated results might make the engineers confused and hinder the prediction of hydrogen storage capacity for a series of new carbon sorbents.

Up to date, various C–H_2 potentials have been proposed in the LJ and Buckingham forms with different parameters. Typically, all these potentials differ largely from each other and remarkable differences are usually observed in numerous simulated results. Although intrinsic differences between theoretical modeling and experimental conditions are inevitable, identifying the reliability of the C–H_2 potential functions is still of great importance for accurate simulation to guide the experimental research in the hydrogen sorbents field.

Herein, we then aim to search a relatively accurate C–H_2 potential with the first-principles calculations as a criterion to evaluate the interactions between carbon sorbents and hydrogen molecules. A new DFT functional vdw-DF2 [19] that well accounting for dispersion interactions is employed in the calculations and we expect to make a good compensation for the well-known shortage of describing weak dispersive interactions in the traditional DFT calculations [20]. This newly fitted potential function is then used to compare with three different widely used C–H_2 potential functions and evaluate the computational accuracies. To avoid other unwanted effects on the potential comparisons, a pure carbon sample (graphene) is used as host. Graphene has been proved to have high hydrogen storage capacity with large surface area compared with a variety of carbon materials, and is easy to model in theoretical calculations. This would help us to better understand the originations existing in the hydrogen storage capacity evaluations by using different C–H_2 potential functions.

Our investigations show that both LJ and Buckingham formulas are inadequate for the graphene–H_2 interaction potentials due to the mismatch in the attractive and repulsive parts; while our formula can produce excellent fit to the DFT–vdW results. The LJ form potential functions proposed by Wang et al. and the functions taken from Dreiding force field are found having an underestimate for the simulated hydrogen storage capacity due to its weak C–H_2 interaction energy. While the Buckingham form potential functions proposed by Patchkovskii are found having an overestimate due to its short stable adsorption distance. Studies also show that the adsorption sites and hydrogen molecule orientations have large influences on the graphene–H_2 interactions and fitting an accurate C–H_2 potential function from quantum calculations might be a reasonable way to rationally predict the storage capacity of carbon-based hydrogen storage materials.

Models and methods

In order to find our own C–H_2 potential function, a DFT–vdW calculation is performed for a hydrogen molecule adsorbed onto the surface of graphene (Fig. 1). Considering the random distribution and orientation of hydrogen molecules on the

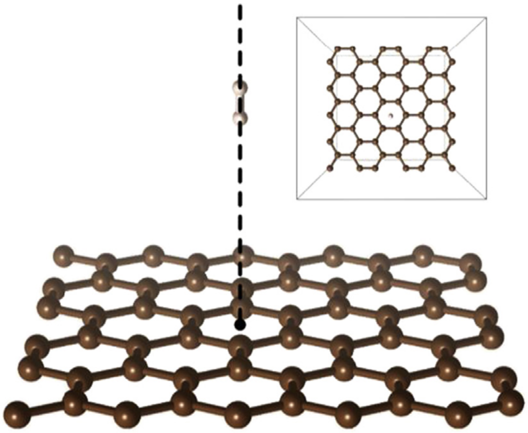

Fig. 1 – Schematic diagram of H_2 adsorption onto the graphene surface. Nine different adsorption configurations are considered and here the H_2 molecule is oriented with the H_2 bond perpendicular to the plane of the graphene and centered at the middle of a hexagon as a clear example.

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