

# Isotropic Potential Model of Hydrogen Physisorption on Exohedral of Single Walled Carbon Nanotubes with Various Diameter

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**Abstract.** This work presents step-by-step procedure of modeling accurate interaction potential energy between hydrogen and outer surface of zigzag Single Walled Carbon Nanotube (CNT) as a function of its diameter. First principles calculations at MP2 method level and def2-SVP basis-set were performed to predict the interaction potential energy of hydrogen gas molecule on outer surface of CNT cluster model. The result shows that the physisorption energy is ranging between 1.05 kcal/mol to 1.14 kcal/mol. Using force-matching method, Lennard-Jones potential parameters were approximated for interaction between united-atom model of hydrogen molecules and the CNT. Assuming constant  $\sigma = 3.2 \text{ \AA}$ , the result shows that the  $\epsilon$  parameter can be defined as a function of CNT diameter.

**Keywords.** Hydrogen, Carbon Nanotube, First principles, Ab initio, Binding Energy, Force-matching Method, Lennard-Jones Potential

**Abstrak.** Karya ini menyajikan prosedur langkah-demi-langkah pemodelan interaksi energi potensial yang akurat antara hidrogen dan permukaan luar dari zigzag Single Walled Carbon Nanotube (CNT) sebagai fungsi dari diameter. prinsip-prinsip pertama perhitungan di tingkat metode MP2 dan def2-SVP dasar-set dilakukan untuk memprediksi interaksi energi potensial dari molekul gas hidrogen pada permukaan luar dari model kluster CNT. Hasilnya menunjukkan bahwa energi physisorption berkisar antara 1,05 kkal/mol menjadi 1,14 kkal/mol. Dengan menggunakan metode kekuatan-matching, Lennard-Jones parameter potensial didekati untuk interaksi antara model yang bersatu-atom dari molekul hidrogen dan CNT. Dengan asumsi konstan  $\sigma = 3,2 \text{ \AA}$ , hasilnya menunjukkan bahwa parameter  $\epsilon$  dapat didefinisikan sebagai fungsi dari diameter CNT.

**Kata kunci.** Hydrogen, Carbon Nanotube, First principles, Ab initio, Binding Energy, Force-matching Method, Lennard-Jones Potential

## Introduction

Hydrogen fuel-cell powered vehicle technology is projected as one of solutions for urban air pollution crisis (Cheng, 2001; Veziroglu, 1992; Veziroglu, 2008). United States Department of Energy (DoE) has been conducting many research projects in this field to make it possible to be implemented. One of its concerning is to develop light and compact hydrogen storage technology. Since hydrogen gas has low density in ambient state, it will consume too large space unless it is compressed in high pressure or condensed in low temperature. Traditionally, hydrogen gas can be stored with some different methods: high-pressure tanks (Zheng, 2012), cryogenic tanks (Ledesma-orozco, 2010), metal hydride (Sakintuna, 2007), and chemically bonded in covalent or ionic compound (Lin, 2009). These methods still have some problems such as: unsafe issues caused by high pressure, low storage efficiency caused by high operational cost of low temperature storage technology, and expensive material.

Unsafe issues and low storage efficiency problems can be solved if we can store same amount of hydrogen in lower pressure and as close as possible to ambient temperature. This can be done by adding adsorbent material to the storage tanks. The existence of adsorbent material may attract hydrogen gas molecules to attach on its surface. Many researches have been done to find the best adsorbent material to store hydrogen gas molecules. One of its promising candidates is Carbon Nanotubes (CNTs). Its capability to store hydrogen was first investigated by Dillon (1997). Dillon stated that CNTs are able to store hydrogen gas up to 10 wt% at room temperature. This result inspired further researches all over the world. Yet the other experimental and theoretical researches' results didn't agree with Dillon's result. Liu (1999) stated that their synthesized Single Walled Carbon Nanotubes (SWCNTs) were only able to store up to 2.4 wt% hydrogen gas at ambient temperature and pressure of 100 - 120 bar. Even after heat treatment on the SWCNTs, the hydrogen uptake was only increased to 4.2 wt%. More recent research by Xu (2006) stated that the hydrogen uptake is much lower than Dillon's and Liu's works. At ambient temperature of 303 K and pressure of 100 bar, the hydrogen uptake was only 0.31-0.48 wt%.

These irreproducible results were due to the limitation of experimental instruments and the purity variation among the synthesized CNTs that affect the specific surface area of the CNTs. Therefore, for validating the result of experimental researches, many theoretical studies have been performed to analyze the phenomena of hydrogen adsorption on CNT. Since the equilibrium properties really depend on the activation energy of hydrogen gas desorption on CNT, first principles or density functional theory (DFT) calculations are needed to calculate the interaction potential energy. Li et al. (2003) performed DFT calculations for estimating hydrogen physisorption on CNT. The results show that hydrogen physisorption energy is about 1.8 kcal/mol. Due to the difficulty of the calculations and the limitation of DFT in accounting Van der Waals interactions, Li suggested other researchers to perform first principle calculations to resolve this issue and to get more accurate interaction potential energy.

Besides first principles calculations, classical simulations - such as Molecular dynamics (MD) and grand canonical monte carlo (GCMC) simulations - are also commonly used to predict equilibrium properties of hydrogen gas physisorption on Carbon Nanotube (CNT). In classical simulations, the results very depend on the intermolecular potential energy model used. MD and GCMC may use empirical potential or first-principles derived potential model. Empirical potential is approximated to fit the physical properties provided by simulation with the real fluid's properties, whereas first-principles derived potential is approximated to fit with the interaction potential energy that is calculated from first-principles or DFT calculations. The latter potential can be obtained from force-matching method that is proposed by Ercolessi et al. (1994).

Using force matching method, molecule can be modeled into isotropic model (also known as united atom model) and anisotropic model. In isotropic model, the interaction between molecules is determined as the function of molecular center distance regardless the orientations of the interactions, in other word, the orientation effects are neglected. In 1994, Buch (1994) proposed isotropic model of hydrogen molecule that was able to accurately reproduce the physical properties of hydrogen, but it was inaccurate for high density or low temperature because of hydrogen anisotropic quadrupole-quadrupole interactions.

Compared to isotropic model, anisotropic model is usually better in producing accurate physical and thermodynamics properties of fluid. Anisotropic model just differ with isotropic model in existence of partial charge. In anisotropic model – e.g. in anisotropic model of hydrogen molecule proposed by McLaughlin et.al. (2012) – the atomic center is usually assigned as positive partial charge, while the electron cloud is assigned as negative partial charge. The electron representation is usually assigned with fictitious mass when implemented in MD simulations in order to prevent it moving too far away from the molecule (Tangney, 2006). Anisotropic model of hydrogen molecule was proposed as well by Belof et al. (2007; 2008; 2009) to be implemented for theoretical study of hydrogen sorption on metal organic framework (MOF) with highly accurate result.

Even though anisotropic model is superior to isotropic model, isotropic model is still considered and implemented in many MD and GCMC simulations (Huarte-Larranaga, 2007; Banerjee, 2008). Yet, the technical uses of the potential were often not as it should be, e.g. the potential designed for united atom model of hydrogen was often mistakenly used for diatomic model. Consequently, the intermolecular potential energy model was not correct and the simulation would give inaccurate physical and thermodynamics properties of the system. Therefore, careful treatments are needed whenever isotropic model is implemented.

In case of hydrogen physisorption on CNT, isotropic model usually fails in accounting effect of CNT curvature to the hydrogen physisorption energy, otherwise the potential function parameter is set as function of the CNT diameter (Knippenberg, 2008). In 2002, Kostov et.al. (2002) proposed potential parameter of hydrogen-carbon interaction as a function of the CNT curvature. The disadvantage of Kostov work was that they took the potential parameter from existing intermolecular potential that was not yet to be tested. Kostov also performed DFT calculations by using the hybrid B3LYP functional that is usually not as accurate as ab initio calculations. Therefore, in order to get more accurate potential model of hydrogen physisorption on CNT, this work performed step by step procedure - from ab-initio calculations to force matching method - to obtain potential function parameter as a function of the CNT diameter.

Similar work was performed by Mahdizadeh et.al. (2014) for hydrogen molecular interaction with CNT, silicon nanotube (SiNT), and silicon-carbide nanotube (SiCNT). However, their work was still limited for two variations of CNT diameter, (19,19) CNT and (11,11) CNT. Therefore, the aim of the present work is to calculate hydrogen physisorption energy on CNT with wider range of diameter and to be able to approximate the potential parameter as a function of its diameter. In this work, we provide accurate potential model to be implemented by any researches on molecular dynamics or monte carlo simulations in future.

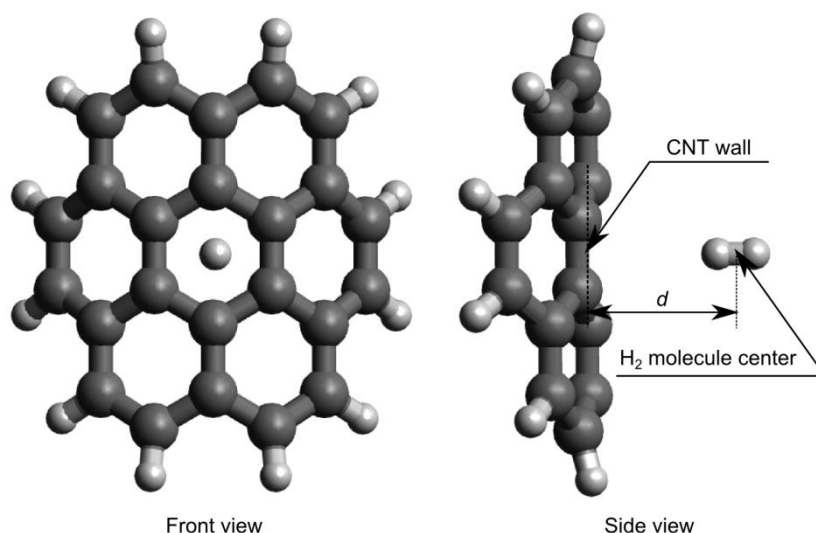
## **Computational Details**

### *First-principle study*

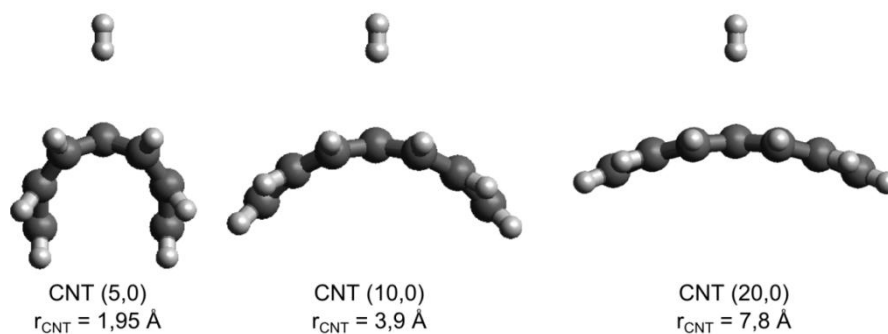
We calculate interaction potential energy of hydrogen molecule and CNT using ab-initio calculations performed at MP2 method level (Møller, 1934) and def2-SVP basis-sets (Eichkorn, 1997) performed with PSI4 package (Turney, 2011). The CNT structure is simplified into cluster model like shown on fig-1 in order to reduce the computational cost. In this cluster model, the CNT is simplified into only 24 carbon atoms that is close to the hydrogen molecule, while the further atoms are neglected due to their little contribution to the interaction potential energy with the hydrogen

molecule. All carbon atoms located on the edge of the model are saturated with hydrogen atoms to make the system in closed-shell configuration which is more stable for electronic structure calculations. Several previous works have used similar models and stated that it could give accurate results (Mahdizadeh, 2014; Lithoxoos, 2008).

In this first-principle study, we calculate several single-point energy calculations in various distance between the wall of nanotube and molecular center of hydrogen. The hydrogen molecule is placed in perpendicular orientation above the center of hexagonal structure of CNT (hollow site),



**Figure 1** Cluster model of hydrogen physisorption on CNT (10,0) for first-principle study to calculate interaction potential energy in perpendicular orientation.



**Figure 2** CNT with various chirality and radius.

since it is the place where the strongest interaction configuration between hydrogen molecule and CNT occurs. The illustration is shown in fig-1. The interaction potential energy between hydrogen and CNT is calculated using the following equation:

$$\Delta E = E_{H_2-CNT} - (E_{CNT} + E_{H_2}) \quad (1)$$

We calculate interaction potential energy of hydrogen and CNT in various diameter by varying the chirality of the CNT. Since the smallest CNT that can be synthesized is 3 Å, we choose: (5,0) zigzag-CNT with diameter of 3.9 Å. Several CNTs with larger chirality and diameter are also investigated in order to get sufficient amount of data for regression (see fig-2).

### Force-matching method

We use force-matching method to approximate interaction potential parameter of carbon and hydrogen molecule. Hydrogen molecule is modeled into isotropic or united atom model. The hydrogen atoms on the edge of CNT cluster model are neglected in force-matching calculation in assumption that it doesn't contribute much to the interaction potential energy (see fig 3).

We use Lennard-Jones (LJ) potential function to define non-covalent interatomic potential energy between carbon atom and hydrogen molecule (C-H<sub>2</sub>), as the following equation:

$$\Delta E_{C-H_2} = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (2)$$

Then, the interaction potential energy between CNT and hydrogen molecule are calculated by summing the interaction potential energy of hydrogen molecule with 24 carbon atoms in the model. Therefore, we use the following equation:

$$\Delta E_{CNT-H_2} = 4\varepsilon \sum_{i=1}^{24} \left[ \left( \frac{\sigma}{r_i} \right)^{12} - \left( \frac{\sigma}{r_i} \right)^6 \right] \quad (3)$$

### Modeling potential parameter as a function of CNT diameter

By assuming that  $\sigma$  parameter is not influenced by the curvature of CNT, we apply same  $\sigma$  parameter for all diameter of CNT. We choose  $\varepsilon$  parameter as the only variable that is affected by the curvature of CNT. For modeling potential parameter as a function of CNT diameter, we propose a quite different equation with previous equation that was proposed by Kostov. While Kostov used potential parameter of hydrogen with carbon in  $sp_3$  (diamond) and  $sp_2$  (graphite) hybridization configurations as the operation range limit of their equation, we choose to use potential parameter of hydrogen with carbon in the smallest diameter (5,0) CNT and  $sp_2$  as the operation range limit of our equation. We propose the following equations:

$$\varepsilon(D) = \varepsilon_{(5,0)} f(D) + \varepsilon_{sp_2} [1 - f(D)] \quad (4)$$

$$f(D) = \left( \frac{D_{(5,0)}}{D} \right)^n \quad (5)$$

Since the curvature of CNT is similar to graphite,  $D \rightarrow \infty$  leads  $f(D) \rightarrow 0$ , and consequently  $\varepsilon(D) \rightarrow \varepsilon_{sp_2}$ . Oppositely,  $D \rightarrow D_{(5,0)}$  leads  $f(D) \rightarrow 1$ , and consequently  $\varepsilon(D) \rightarrow \varepsilon_{(5,0)}$ . These equations are modification from Kostov equations ([Kostov, 2002](#)). In the next section of this paper, we explain the reason behind this modification.

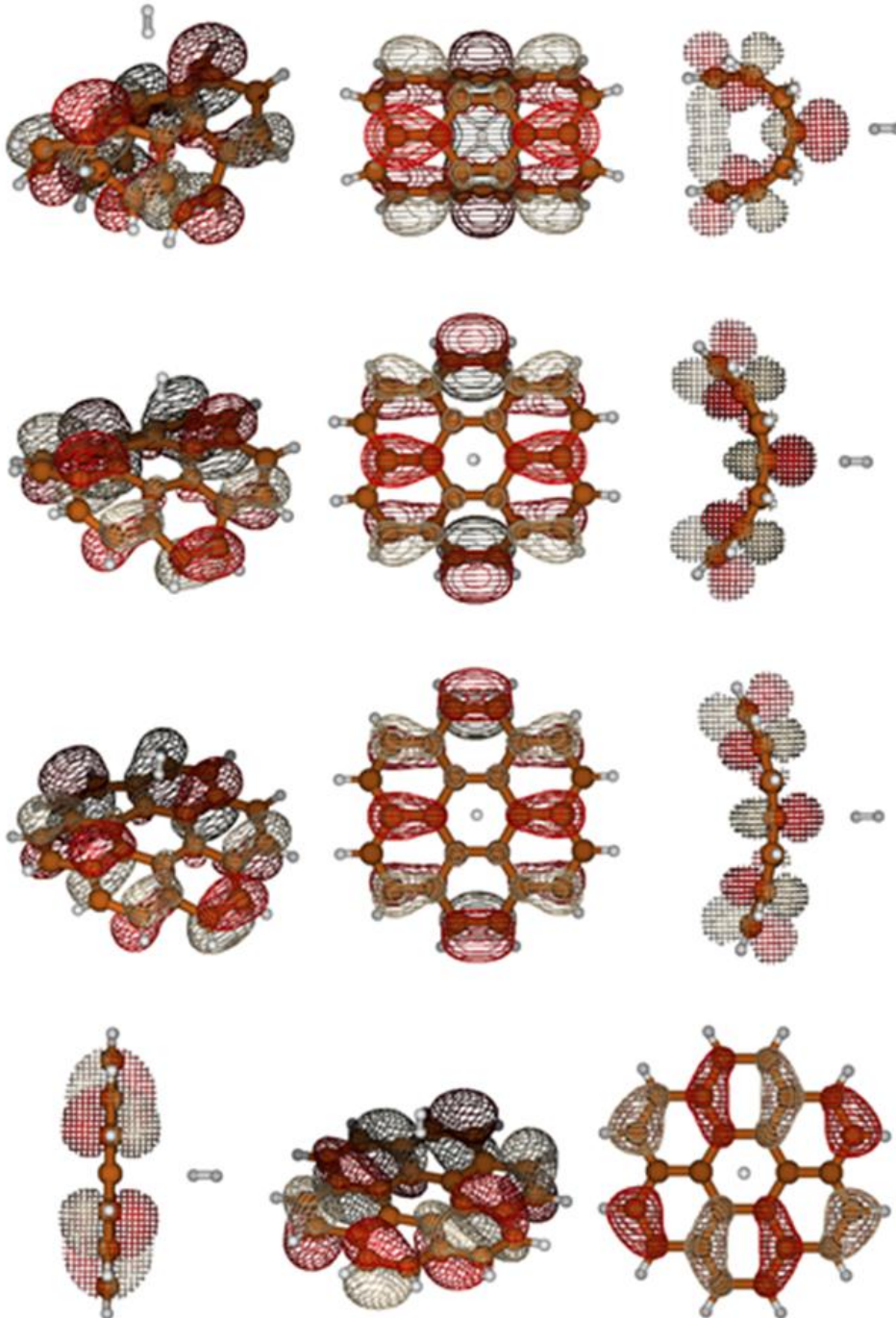
## Results and Discussions

Fig-4 visualizes the isosurface for highest occupied molecular orbital (HOMO) visualization for hydrogen molecule interaction with (5,0), (10,0), (20,0) CNT, and graphene. These visualization show that the curvature of carbon structure affects the molecular orbital shape. The differences on molecular orbital shape result the differences on interaction potential energy between the CNT and

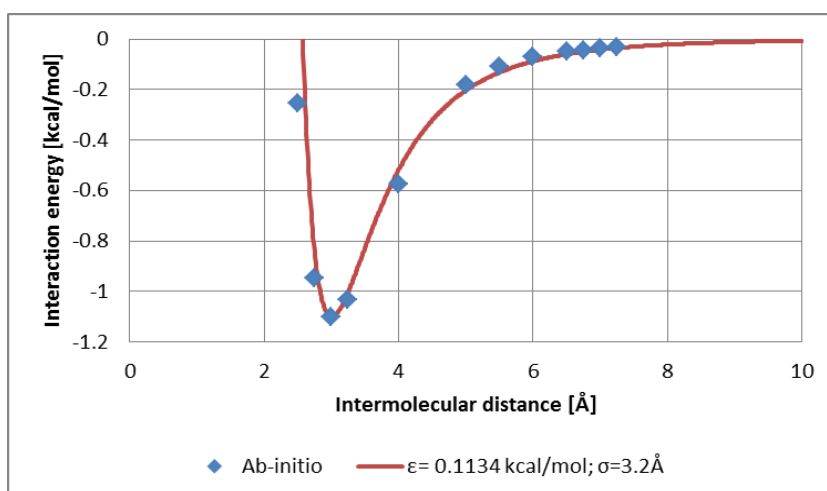
the hydrogen molecule as well. The results of interaction potential energy calculations and force-matched potential for (5,0), (10,0), and (20,0) CNT are shown on fig-5, fig-6, fig-7. The results for other diameter variations of CNT are shown on fig-8 and table-1.

The results of force-matched potential parameter show a good trend that could be matched into an equation. Using equation (4) and (5), we do a regression technique by modifying the equation (4) and (5) become the following equation:

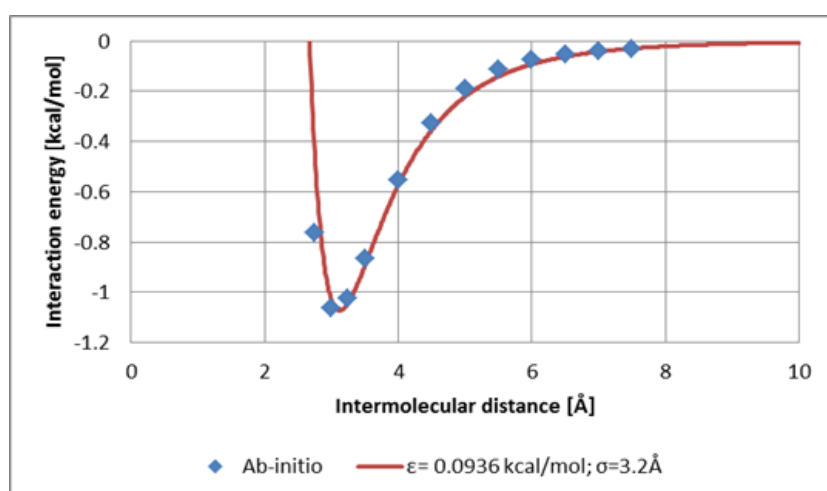
$$\frac{\varepsilon(D) - \varepsilon_{sp_2}}{\varepsilon(5,0) - \varepsilon_{sp_2}} = f(D) = \left( \frac{D(5,0)}{D} \right)^n \quad (6)$$



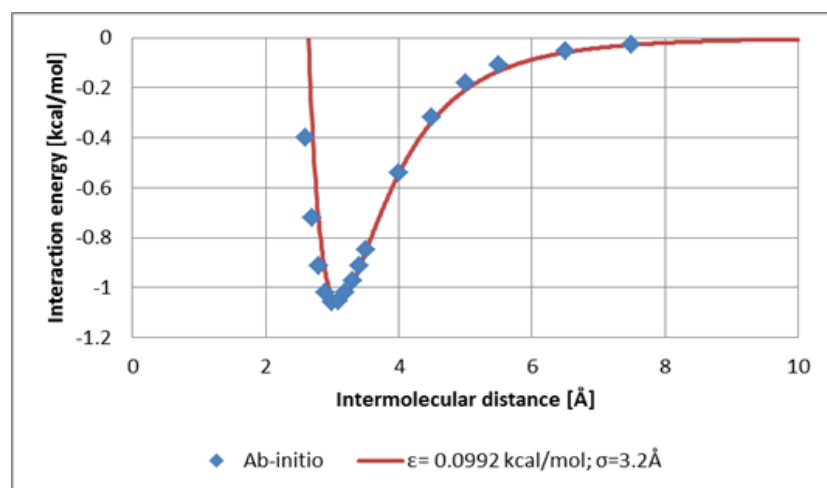
**Figure 4** Isosurface (electron density: 0.02 u.a.) for highest occupied molecular orbital of respectively from top to bottom (5,0), (10,0), (20,0), and (1280,0) CNT model (quite similar with graphene structure) interacting with hydrogen molecule: 3D view, front view, and side view.



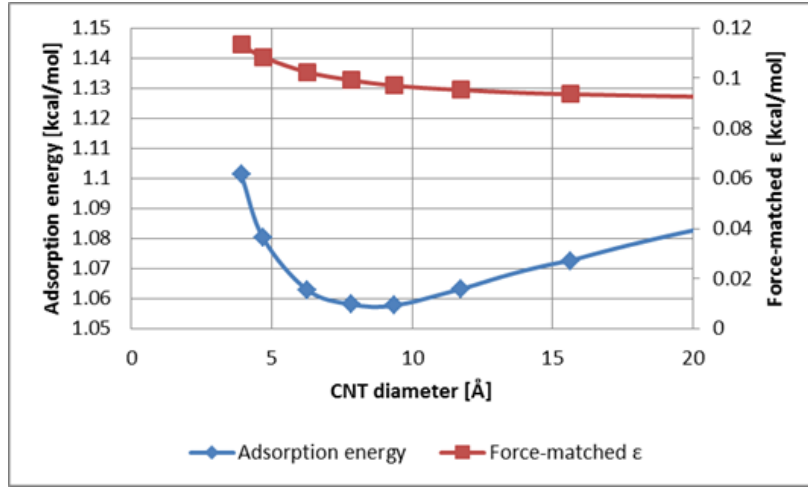
**Figure 5** Ab-initio calculation and force-matching result for hydrogen physisorption on (5,0) CNT



**Figure 6** Ab-initio calculation and force-matching result for hydrogen physisorption on (10,0) CNT.



**Figure 7** Ab-initio calculation and force-matching result for hydrogen physisorption on (20,0) CNT.



**Figure 8** Ab-initio calculation and force-matching results for hydrogen physisorption on various diameter of CNT.

**Table 1** Ab-initio calculation and force-matching results for hydrogen physisorption on various diameter of CNT.

Diameter [Å]	Adsorption energy [kcal/mol]	Force-matched ε [kcal/mol]
3.909	1.101	0.1134
4.69	1.080	0.1084
6.254	1.063	0.1024
7.817	1.058	0.0992
9.38	1.057	0.097
11.726	1.063	0.0953
15.634	1.073	0.0936
∞ (Graphene)	1.142	0.0899

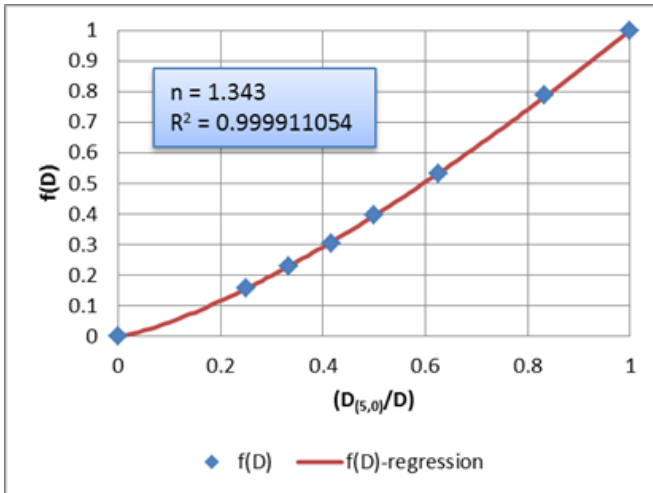
Based on first-principle study result, the value of the constants on equation (6) are listed on table-2. By equation fitting technique, we approximate the value of variable n. The regression result is shown in fig-9. We get the value of variable n = 1.343 could fit the data with coefficient of determination up to 0.999.

Using same technique, we approximate the value of variable n for Kostov equations ([Kostov, 2002](#)):

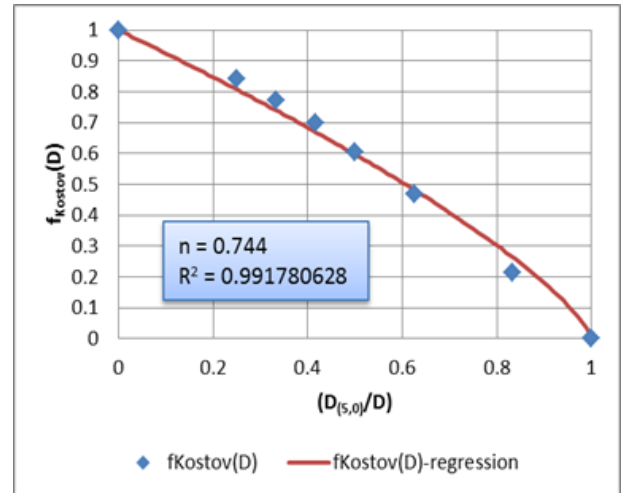
$$\varepsilon(D) = \varepsilon_{(5,0)}[1 - f(D)] + \varepsilon_{sp_2}f(D) \quad (7)$$

$$f(D) = \left(1 - \frac{D_{(5,0)}}{D}\right)^n \quad (8)$$





**Figure 9** Equation fitting for approximating the best match variable  $n$  on equation (6).



**Figure 10** Equation fitting for approximating the best match variable  $n$  on Kostov equation (8).

The regression result for Kostov equation is shown in fig-10. We get the value of variable  $n = 0.744$  could fit the data with coefficient of determination only about 0.991. Based on this results, we confidentially proof that our proposed equations are better than Kostov equation in providing accurate potential parameter as a function of CNT diameter.

**Table 2** Constants value for equation (6)

Constant	Value	Unit
$D_{(5,0)}$	3.909	Å
$\mathcal{E}_{(5,0)}$	0.1134	kcal/mol
$\mathcal{E}_{sp2}$	0.0899	kcal/mol

## Conclusions

This first-principle study of hydrogen physisorption on various diameter of CNT shows that the curvature of CNT affects the hydrogen physisorption energy. The influence is not too significant to the value of the hydrogen physisorption energy, it is only varying around 1.05 – 1.14 kcal/mol ( $\pm 8\%$ ). However, the influence on potential parameter is quite significant, it is varying from 0.0899 – 0.1134 kcal/mol ( $\pm 24\%$ ). Based on this results, we conclude that using accurate potential parameter is very essential, and it can be achieved using our diameter-dependent potential parameter equation with considerable accuracy.

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## References

- [1] Banerjee S, Puri IK (2008) Enhancement in hydrogen storage in carbon nanotubes under modified conditions. *Nanotechnology*. 19(15):155702. doi:10.1088/0957-4484/19/15/155702.

- [2] Belof JL, Stern AC, Eddaoudi M, Space B (2007) On the mechanism of hydrogen storage in a metal-organic framework material. *Journal of the American Chemical Society*. 129(49):15202-15210. doi:10.1021/ja0737164.
- [3] Belof JL, Stern AC, Space B (2008) An accurate and transferable intermolecular diatomic hydrogen potential for condensed phase simulation. *Journal of Chemical Theory and Computation*. 4(8):1332-1337. doi:10.1021/ct800155q.
- [4] Belof JL, Stern AC, Space B (2009) A predictive model of hydrogen sorption for metal-organic materials. *Journal of Physical Chemistry C*. 113(21):9316-9320. doi:10.1021/jp901988e.
- [5] Buch V (1994) Path integral simulations of mixed para-D<sub>2</sub> and ortho-D<sub>2</sub> clusters: The orientational effects. *Journal of Chemical Physics*. 100(10):7610-7629. doi:10.1063/1.466854.
- [6] Cheng HM, Yang QH, Liu C (2001) Hydrogen storage in carbon nanotubes. *Carbon*. 39(10):1447-1454. doi:10.1016/S0008-6223(00)00306-7.
- [7] Dillon AC, Jones KM, Bekkedahl TA, Kiang CH, Bethune DS, Heben MJ (1997) Storage of hydrogen in single-walled carbon nanotubes. *Nature*. 386(6623):377-379. doi:10.1038/386377a0.
- [8] Eichkorn K, Weigend F, Treutler O, Ahlrichs R (1997) Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials. *Theoretical Chemistry Accounts*. 97(1-4):119-124. doi:10.1007/s002140050244.
- [9] Ercolessi F, Adams JB (1994) Interatomic Potentials from First-Principles Calculations: The Force-Matching Method. *Europhysics Letters*. 26(8):583. doi:10.1209/0295-5075/26/8/005.
- [10] Huarte-Larranaga F, Alberti M (2007) A molecular dynamics study of the distribution of molecular hydrogen physisorbed on single walled carbon nanotubes. *Chemical Physics Letter*. 445(4-6):227-232. doi:10.1016/j.cplett.2007.07.083.
- [11] Knippenberg MR, Stuart SJ, Cheng H (2008) Molecular dynamics simulations on hydrogen adsorption in finite single walled carbon nanotube bundles. *Journal of Molecular Modeling*. 14(5):343-351. doi:10.1007/s00894-008-0275-2.
- [12] Kostov MK, Cheng H, Cooper AC, Pez GP (2002) Influence of carbon curvature on molecular adsorptions in carbon-based materials: A force field approach. *Physical Review Letters*. 89(14):146105. doi:10.1103/PhysRevLett.89.146105.
- [13] Ledesma-orozco E, Aceves SM, Espinosa-loza F (2010) Development of dual volume cryogenic hydrogen storage system. *ASME International Mechanical Engineering Congress and Exposition, Proceedings (IMECE)*. 3(PARTS A AND B):797-804. doi:10.1115/IMECE2010-39795.
- [14] Li J, Furuta T, Goto H, Ohashi T, Fujiwara Y, Yip S (2003) Theoretical evaluation of hydrogen storage capacity in pure carbon nanostructures. *Journal of Chemical Physics*. 119(4):2376-2385. doi:10.1063/1.1582831.
- [15] Lin Y, Mao WL, Mao HK (2009) Storage of molecular hydrogen in an ammonia borane compound at high pressure. *Proceedings of the National Academy of Sciences of the United States of America*. 106(20):8113-8116. doi:10.1073/pnas.0903511106.
- [16] Lithoxoos GP, Samios J (2008) Investigation of Silicon Model Nanotubes as Potential Candidate Nanomaterials for Efficient Hydrogen Storage: A Combined Ab Initio/Grand Canonical Monte Carlo Simulation Study. *Journal of Physical Chemistry C*. 112(43):16725-16728. doi:10.1021/jp805559a.
- [17] Liu C, Fan YY, Liu M, Cong HT, Cheng HM, Dresselhaus M S (1999) Hydrogen storage in single-walled carbon nanotubes at room temperature. *Science*. 286(5442):1127-1129. doi:10.1126/science.286.5442.1127.
- [18] Mahdizadeh SJ, Goharshadi EK (2014) Hydrogen storage on silicon, carbon, and silicon carbide nanotubes: A combined quantum mechanics and grand canonical Monte Carlo Simulation study. *International Journal of Hydrogen Energy*. 39(4):1719-1731. doi:10.1016/j.ijhydene.2013.11.037.

- [19] McLaughlin K, Cioce CR, Belof JL, Space B (2012) A molecular H<sub>2</sub> potential for heterogeneous simulations including polarization and many-body van der Waals interactions. *Journal of Chemical Physics*. 136(19):194302. doi:10.1063/1.4717705.
- [20] Møller Chr, Plesset MS (1934) Note on an Approximation Treatment for Many-Electron Systems. *Physical Review*. 46:618. doi:10.1103/PhysRev.46.618.
- [21] Sakintuna B, Lamari-Darkrim F, Hirscher M (2007) Metal hydride materials for solid hydrogen storage: A review. *International Journal of Hydrogen Energy*. 32(9):1121-1140. doi:10.1016/j.ijhydene.2006.11.022.
- [22] Tangney P (2006) On the theory underlying the Car-Parrinello method and the role of the fictitious mass parameter. *Journal of Chemical Physics*. 124(4):044111. doi:10.1063/1.2162893.
- [23] Turney JM, Simmonett AC, Parrish RM, Hohenstein EG, Evangelista FA, Ferman JT, *et.al.* (2011) Psi4: an open-source ab initio electronic structure program. *WIREs Computational Molecular Science*. 2(4):556-565. doi:10.1002/wcms.93.
- [24] Veziroglu TN, Barbir F (1992) Hydrogen: the wonder fuel. *International Journal of Hydrogen Energy*. 17(6):391-404. doi:10.1016/0360-3199(92)90183-W.
- [25] Veziroglu TN, Sahin S (2008) 21st Century's energy: hydrogen energy system. *Energy Conversion Management*. 49(7):1820-1831. doi:10.1016/j.enconman.2007.08.015.
- [26] Xu WC, Takahashi K, Matsuo Y, Hattori Y, Kumagai M, Ishiyama S, *et al.* (2006) Investigation of hydrogen storage capacity of various carbon materials. *International Journal of Hydrogen Energy*. 32(13):2504 – 2512. doi:10.1016/j.ijhydene.2006.11.012.
- [27] Zheng J, Liu X, Xu P, Liu P, Zhao Y, Yang J (2012) Development of high pressure gaseous hydrogen storage technologies. *International Journal of Hydrogen Energy*. 37(1):1048-1057. doi:10.1016/j.ijhydene.2011.02.125.