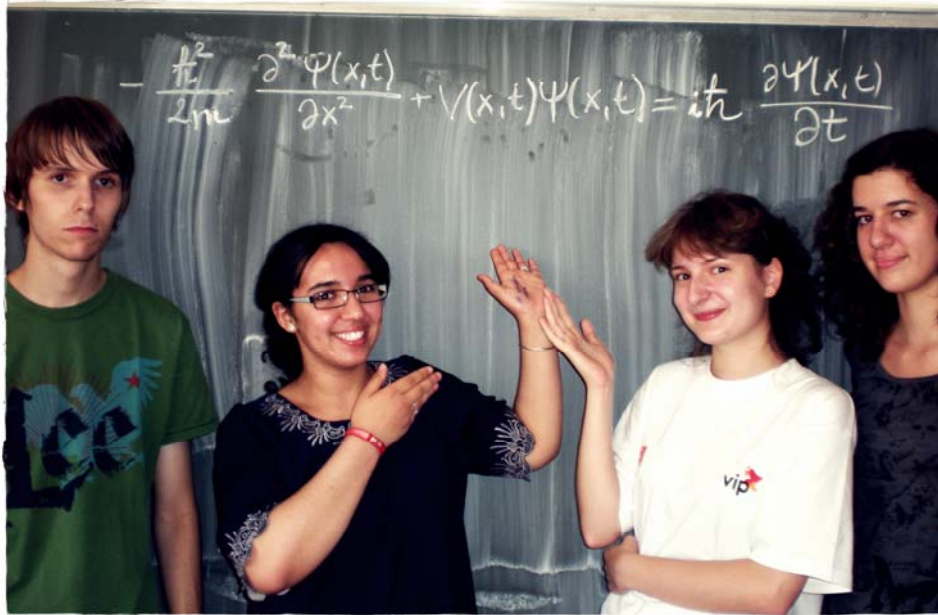


Will hydrogen be caged in your future fuel tank?



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Introduction

Hydrogen is a highly reactive, invisible, tasteless, colorless gas, the lightest element in the universe, fuel of galaxies and stars. Even 150 years ago there were ideas that hydrogen can be used as an energy source:

“Pencroft: ‘And what will they burn instead of coal?’ Harding: ‘Water. But water decomposed into its primitive elements... yes, my friends, I believe that water will some day be employed as fuel, that hydrogen and oxygen which constitute it... will furnish an inexhaustible source of heat and light... Some day water will be the coal of the future.’”

Jules Verne, *The Mysterious Island*, 1874.

With the concerns regarding the emission of CO₂, greenhouse effect and other environmental issues hydrogen is today considered to be a potential solution to the problem of increasing energy needs. When hydrogen reacts with oxygen in a fuel cell to produce energy, only water is formed as byproduct. The first hydrogen cars have already been designed in which hydrogen is stored in tanks as liquid under high pressures and/or low temperatures. However, it takes a significant amount of energy and money to pressurize the gas, which detracts from the efficiency of the hydrogen economy [1]. Also there is still work to be done on safety issues as hydrogen is highly explosive in mixture with air.

There are two major problems the hydrogen research projects are facing:

1. finding economical ways of making the hydrogen since currently it is mostly obtained from hydrocarbons we get from fossil fuels, *i.e.* methane
2. discovering how to store hydrogen efficiently under near-ambient conditions

Our group concentrated on the second goal and using computational methods explored the hydrogen storage capacity of different nanoporous materials: carbon nanotubes, fullerenes and clathrate hydrates (see Figure 1). The project was conducted in two steps. The first one was to explore the nature of interactions between the hydrogen molecules and different host materials. The second goal was to find the energy (stability) of the systems with various number of hydrogen molecules. Based on this we were able to conclude about the viability of given materials to store different amounts of hydrogen.

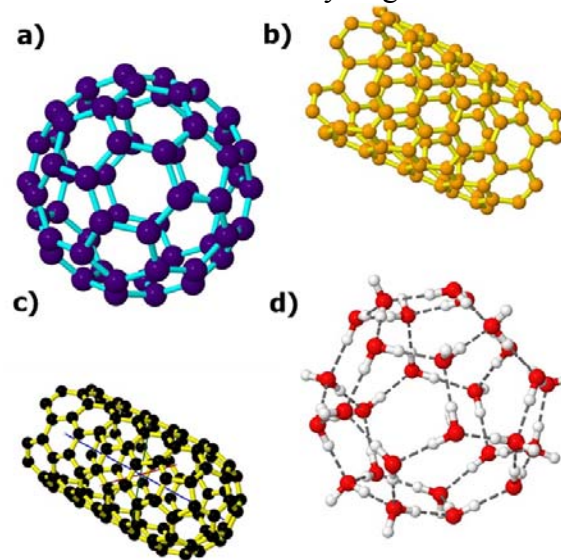


Figure 1. Some of the investigated systems: a) C_{60} fullerene, b) open armchair (5,5) nanotube c) capped armchair (5,5) nanotube d) hydrogen hydrate

Computational methods

In the first part of the project we wrote a computer program in order to calculate the Lennard-Jones potential which describes the Van der Waals interactions between the host material and hydrogen molecule. The optimized parameters for the potential were taken from S. Alavi *et al.* and M. Xu *et al.* [2,3]. The potential for the interaction of hydrogen with the large cage of hydrogen hydrate is shown in Figure 2 as an example. The investigated potentials are used in the second part of the project.

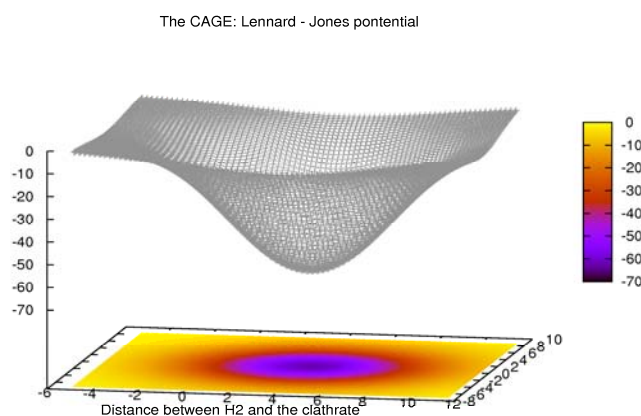


Figure 2. Lennard-Jones potential for hydrogen molecule inside the big cage of sII clathrate hydrate. The energy is given in cm^{-1} .

In the second part we calculated the maximum number of hydrogen molecules that can be absorbed by a particular system. Hydrogen is a quantum object, therefore to determine the energy of our systems we solved the corresponding Schrödinger equation by using a computer program for Diffusion Monte Carlo (DMC). This method solves this famous equation by propagating the hydrogen molecules inside the host structures. Hydrogen molecules in principle move randomly, therefore the method bears Monte Carlo in its name. After each step the molecule is propagated, the potential and total energy are calculated. If the move was energetically beneficial the propagation is continued, if not propagation is stopped. The calculations are repeated certain amount of steps until the molecules concentrate in the regions of low potential energy. We solved the Schrödinger equation for our systems with various number of hydrogen molecules inside. Therefore, we were able to determine if our system is stable or not and how the number of hydrogen molecules affects the overall stability.

Results and discussion

Single - walled carbon nanotubes (SWNTs)

Carbon nanotubes are molecular-scale tubes of graphitic carbon with outstanding properties. Because of their stiffness and remarkable electronic properties they have invoked large scientific interest in last two decades. Carbon nanotubes also showed promise as an effective hydrogen storage material [4]. Main advantage of carbon nanotubes over standard build tanks is that the hydrogen could be stored in a car tank at room temperature as gas and be extracted with relatively small differences in pressure.

By using DMC we investigated the stability of capped and opened nanotubes with different amounts of hydrogen. Figure 3a. shows the calculated energy of the system as a function of the number of hydrogen molecules. Both nanotubes proved to be very good material for storing because hydrogen can be adsorbed inside and outside the tube. We found out that capped tube of 10 Å long can store four hydrogen molecules inside. The other molecules are absorbed on the outer side of the tube. As can be seen from the Figure 3b by adding more hydrogen the energy of the system decreases and thus the system becomes even more stable.

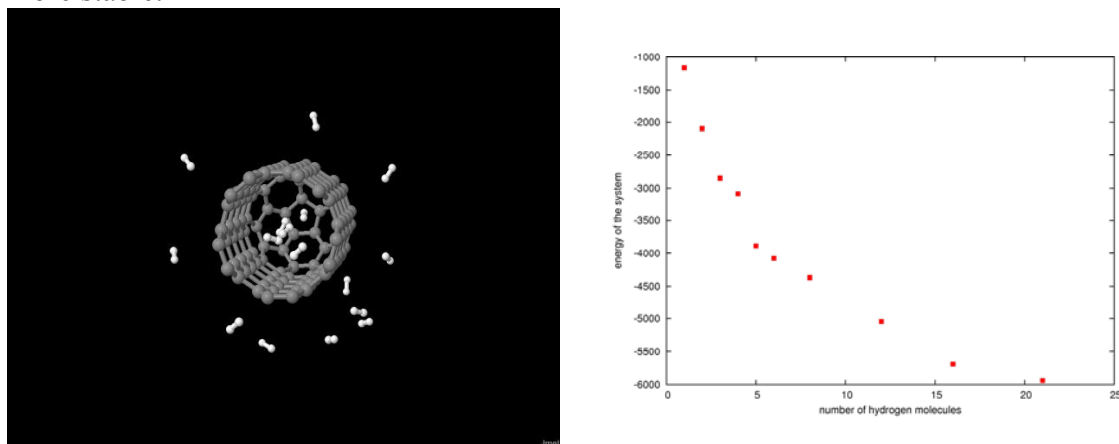


Figure 3. a) DMC simulation for 16 H₂ molecules inside the capped armchair (5,5) nanotube b) the dependence of the total energy of the nanotube on the number of absorbed H₂ molecules

Multi – walled carbon nanotubes (MWNTs)

Multi – walled nanotubes consist of multiple layers (concentric tubes) of graphite. In our project we concentrated on a specific type of MWNTs – double – walled carbon nanotubes. According to scientists from Japan, USA and Mexico DWNTs have proven to have higher thermal and chemical stability. However their morphology and properties still remain similar.

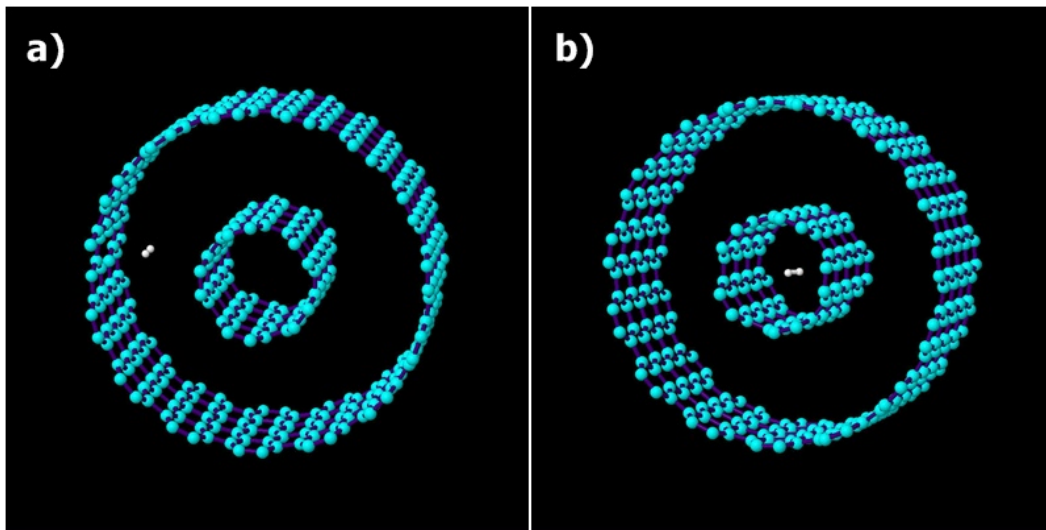


Figure 4. a) The initial condition for hydrogen propagation in DWNT by DMC method
b) The final position of the lowest energy

By using DMC method we investigated the behaviour of the hydrogen molecule between the two layers in DWNT. Different distances between two layers were explored and it was found that all variations had the same final result. As can be seen from Figure 4. the molecule did not find its lowest energy between the layers, on the contrary it moved to the center of the DWNT. This means that when MWNT is being filled with hydrogen, hydrogen will first absorb in the inner nanotube and then will start absorbing between the layers.

Fullerenes

Additional structures that were tested were fullerenes. Fullerenes are a family of carbon allotropes, molecules composed entirely of carbon, structured in the form of a hollow sphere, ellipsoid, or a tube. These structures probably will not be used for hydrogen storage as the internal surface of fullerenes does not open easily for adsorption. Even though our results might not have a practical value, there have been many controversial results about fullerenes capacity for hydrogen. For example, G. Dolgonos *et al.* [5] stated that only one hydrogen molecule being incorporated inside the C_{60} cage can form the stable complex in agreement with geometric considerations and recent experimental data. On the other hand, a recent article of O. V. Pupysheva *et al.* [6] found that a maximum of 58 hydrogen atoms inside a C_{60} cage still remain a metastable structure.

In our research, we calculated the stabilization energy by performing Diffusion Monte Carlo simulations and have determined that smaller fullerenes like C_{60} and C_{72} are stable containing only one hydrogen molecule. For example, the energy of $H_2@C_{60}$ is -1261.2 cm^{-1} and $2H_2@CO_{60}$ is 9841.2 cm^{-1} . When we increase the number of carbon atoms in the cage, the

capacity for hydrogen also increases. C_{78} can store two hydrogen molecules and C_{86} three. The largest fullerene we have tested is C_{180} and it can hold at least five molecules of hydrogen (see Figure 5).

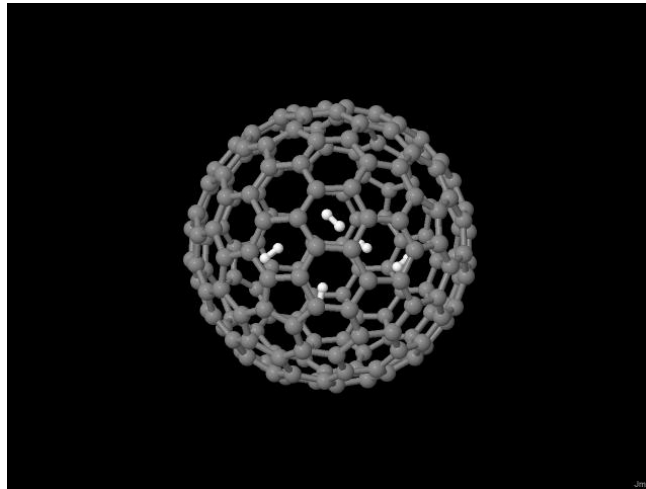


Figure 5. DMC simulation for 5 H_2 molecules inside C_{180}

Clathrate hydrates

Clathrate hydrates are solids in which water molecules linked with hydrogen bonds create cavities that can enclose a large variety of molecules, in our case molecules of hydrogen. As in previous cases, there is no chemical bonding between the host water molecules and hydrogen, however a weak Van der Waals interaction exists. Hydrates are stable at temperatures below as well as above the normal freezing point of water. When empty, these cages are unstable, collapsing into the conventional ice crystal structure.

There are three (common) structure types of clathrate hydrates: sI, sII and sH. The clathrate hydrate unit cell of structure sII is composed out of 16 small and 8 big cages (Figure 6). Investigating the stability of different cages with the DMC method we could conclude that the big cage holds four hydrogen molecules and the small one can hold only one hydrogen molecule. The mass weight of hydrogen per cell unit of clathrate hydrate is thus 3,94%. However the US Department of Energy, which funds a significant amount of research in the field of hydrogen storage has set a goal to reach 6% mass weight of H_2 until 2010 and 9% mass weight H_2 until 2015 [7]. Considering this information and our results we can conclude that clathrate hydrates are not suitable materials for efficient hydrogen storage.

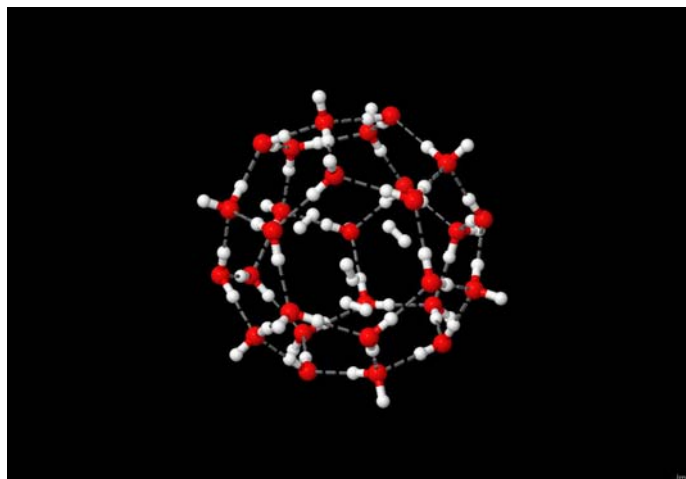


Figure 6. DMC simulation for 4 H₂ inside the large cage of sII hydrogen hydrate

Conclusion

Further research into these issues might bring new materials that would enable safe and efficient on board storage of hydrogen. The methods of computational chemistry will surely have a major role in the discovery and testing of the new materials. Working on this project has introduced us to a whole new perspective of chemistry.

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