Prediction of Materials for Hydrogen Storage: Quantum Chemical Methods and Materials Modeling are Indispensable Tools

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Abstract

The basic understanding of hydrogen molecular interaction with the solid surface is one of the important criterions to design the hydrogen storage materials. Such understanding at the molecular scale can only be achieved by employing appropriate electronic structure methods. Accordingly, the present article reports the theoretical work carried out in our laboratory for designing the hydrogen storage materials. In particular, we demonstrate the theoretical prediction and design of the materials for hydrogen storage using some of the elegant chemical concepts: (a) Ion-Molecule interaction mediated hydrogen adsorption (b) Aromaticity induced hydrogen adsorption (c) Nanoscale curvature induced hydrogen adsorption. The suitability of these complexes for developing fullerene-based hydrogen storage materials is discussed along with the experimental reports.

Introduction

In recent years, it has been unambiguously comprehended that theoretical modeling in many areas of research applied at different scales (matter and time), is being largely practiced and pursued by almost all universities and institutes. The level of confidence that has been accomplished from the accurate predictions and explanations of numerous phenomena by various levels of \textit{ab initio} and phenomenological theories, have transformed the mindset of research groups to the extent that these theoretical tools have now become an indispensable tool like any other sophisticated instruments in a laboratory. Many of the proposed models as well as theoretical methods have together made a profound impact on our understanding of the natural observations at the microscopic and macroscopic levels in an elegant way. These theoretical methods are simply the mathematical methods or models which basically emerge from the fundamental basic laws of science to unravel several phenomena and understand the nature of systems ranging from atomistic scales to mesoscale materials.

Although the successes of theories and associated models are very well known in the literature, the successful predictions heavily rely on the type of systems which are under scrutiny.\textsuperscript{1} For example, the role of theoretical models is inevitable for optimizing the structural design, automotive applications, optimizing several parameters for a specific function, at the mesoscale level, etc. However, applicability of the theoretical models for understanding the physical and chemical systems at the atomistic levels significantly depends to a large extent on the nature of the quantummechanical properties of the particles involved in the system. In this regard, the problem of prediction as well as interpretation of the preferred direction of a chemical reaction and product formation under different conditions is still considered as a great challenge.\textsuperscript{2} Thus, the theoretical models have been classified into two different domains based on the classical and quantum mechanical foundations which are very popular among the engineers and scientists, respectively.

The recently developed theories based on the principles of quantum mechanics applied to the chemistry and physics related problems at the atomistic levels, so called quantum chemical methods provide a basic framework...
to investigate several problems spanning from the nature of bonding in molecular systems; surface phenomena based properties to electronic conductance, magnetism, etc. with a reasonable accurate way.\textsuperscript{3,4} The applicability of these methods has been realized to small-medium sized systems with the precision to the experimental findings. It should also be mentioned that for the case of larger molecular systems, these methods are still prohibitively expensive from the computational point of view. The present article focuses on such theoretical methods which primarily originates from the philosophy of quantum mechanics and these methods categorically forms the basics of electronic structure techniques and materials modeling. These methods essentially provide the description of electrons present in atoms, molecules and solids by approximately solving the Schrödinger equation for the many electron wave functions. Some of the methods have been developed by involving full parameterization or few external parameterization or first principle based methods without any parameterization while solving the Schrödinger equation which are otherwise classified in the literature as molecular mechanics, semi-empirical or ab-initio (meaning “from the beginning”) methods, respectively. The level of approximations involved in the methods defines the accuracy of the predictions and material properties. The exact solution for hydrogen atom and hydrogen-like atoms can be obtained by solving the Schrödinger equation and for any systems other than having more one electron, approximations are warranted which can directly affect the accuracy of the outcome of the results. A reliable accuracy in evaluating the molecular and material properties can be achieved reasonably with \textit{ab initio} methods, namely wave-function theory and density functional theory (DFT).\textsuperscript{3,4}

One of the most well-known types of \textit{ab initio} method is the Hartree-Fock(HF) method which approximates the many electron wave functions into one-electron wave functions by adopting the self-consistent central field approximation and it follows the variational principle. This method is one of the most successful method in describing electronic structure and properties of the many electron systems and the introduced error is almost 5-10 % of the total energy of the system, which is the resultant of coulomb repulsion between the electrons explicitly, known as electron correlation error. Unfortunately, the energy corresponding to the correlation error is almost equivalent to the energy corresponding to the inter- and intra- molecular interaction energy of the molecular systems and most of the chemical phenomena. In addition, it has also been observed that the electron correlation error can severely undermine the electronic properties of molecules and solids. Due to these problems and limitations of HF theory, it has been realized the importance of the formulation of a systematic generalization of the issues pertaining to the electron-correlation problem appropriately. There are basically three different ways, through which the theoretical methods have been developed, viz., configuration interaction (CI), many body perturbation theory (MBPT) and coupled cluster (CC), broadly known as post HF methods.\textsuperscript{5} Although these methods have been very accurate in predicting the electronic structure as well as properties of systems, designing several chemical compounds and explaining most of the physical phenomena, the main disadvantage is that these methods are applicable small to moderate size of the systems due to the high computational cost and they require high amount of computer CPU time, memory, and disk space.

There exists another electronic structure method, known as density functional theory, an alternative theoretical method to handle the problem of heavy computational cost by including the electron correlation problem in an approximate way, by employing density as a functional variable rather than the wave function Since the density is function of 3 variables in contrast to 6N variables dependent wave function, the computational cost for the heavier and large systems can be reduced drastically.\textsuperscript{6} The basis of DFT stems from two basic theorems of Hohenberg-Kohn and the practical approach to the present DFT method is formulated by Kohn and Sham which is similar in structure to the \textit{ab initio} based Hartree-Fock method. Because of this reason, the computational community has witnessed upsurge growth of DFT applications in the recent years. Since the DFT method with various exchange-correlation functionals are available, one has to be cautious in choosing the correct exchange-correlation functional for the given set of problems.

The present work described in this article focuses on both the \textit{ab initio} and DFT based calculations for modeling the suitable materials for hydrogen energy. In what follows, we will first discuss the importance of hydrogen energy and then, computational design of suitable materials for the hydrogen storage using some of the elegant chemical concepts. The experimental
validation on the theoretically proposed materials has also been discussed in the last section.

**Materials for Hydrogen Energy**

It has been known for many years that one of the safest and renewable alternative fuels is hydrogen because of its high abundance, nonpolluting nature and renewable form of future energy sources. It is also one of the most important topics of research due to its potential applications for future energy schemes in comparison to the existing carbonaceous fossil fuels, commonly known as hydrogen economy. In spite of many targeted research work towards the hydrogen economy, one of the major challenging aspects is finding a suitable material for hydrogen storage for automobile applications. The most pre-requisite conditions for the hydrogen-storage materials is to have a high volumetric/gravimetric density with fast kinetics for adsorption and desorption of molecular hydrogen and cost effectiveness of the material. In this regard, extensive research has been initiated toward the development of promising novel materials and eventually many materials have been proposed, viz., carbon nanostructures, metal hydrides, zeolites, metalorganic frameworks, polymers, inorganic-organic framework and clathrate compounds for storing the hydrogen. However, none of these materials has been shown to be practically successful materials. It has been now realized that the basic understanding of hydrogen molecular interaction with the solid surface is one of the important criterions to designing the hydrogen storage materials. Such understanding at the molecular scale can only be achieved by employing appropriate electronic structure methods.

Let us now try to understand why the hydrogen molecule being smallest molecule, is still difficult to design a suitable material for its storage. Since the hydrogen molecule is very stable under normal conditions, it is very difficult to polarize and hence, the influence of any neutral surface on the hydrogen molecule is very small.

It is due to the following reasons: (i) It has fully occupied molecular orbital with large potential energy depth (ii) high HOMO-LUMO gap (iii) high ionization potential (iv) low electron affinity. For the effective hydrogen adsorption, the adsorbent surface should be able to polarize the hydrogen molecule. In general, the physisorption is possible when the adsorbent surface and molecular interaction is through van der Waals interaction for which the corresponding interaction energy is basically proportional to the polarizability of the both gas and solid surface, i.e. \( \text{BE}_{\text{H}_2-\text{solid}} = \text{P}_{\text{H}_2} \times \text{P}_{\text{solid}} \times R^6 \), where, \( R \) is the distance between hydrogen molecule and solid; \( \text{P}_{\text{H}_2} \) and \( \text{P}_{\text{solid}} \) refer to the polarizability of hydrogen and adsorbent solid system, respectively.

Since the polarizability of hydrogen is fixed, the other parameter, polarizability of the adsorbent (\( \text{P}_{\text{solid}} \)) can have a dramatic influence on the interaction with hydrogen molecule. It may also be noted that the highly polarizing surface can polarize the hydrogen molecules to the extent that they can be dissociated into atoms which can bind with the adsorbent surface very strongly. This is type of adsorption, commonly known as chemisorption, which happens with the transition metal surfaces, for e.g. Sc, Ti, Pd, Pt, etc. This process is, on the other hand, unwarranted as it requires more amount of energy for the desorption of hydrogen molecules. Hence, in general, in order to have an efficient storage media along with fast kinetics at ambient conditions, the materials are expected to have the hydrogen adsorption energy in the range of 2-5 kcal/mol. Also a weak non-dissociative hydrogen adsorption is preferred to the stronger binding via hydrogen atomic dissociation over the metal cations.

Based on these observations, we defined some of the prerequisite conditions for the effective hydrogen adsorption, the adsorbing materials should be (a) light weight (b) number of hydrogen molecules should be as high as possible (c) the interaction strength should be moderate (2-5 kcal/mol). Accordingly, we have made an attempt to design suitable hydrogen storage materials and we addressed some of the following issues:

a) Can the alkali metal systems be suitable components of materials for hydrogen storage?

b) Why alkali metals can be more preferred than the transition metal atoms?

c) What is the maximum number of hydrogen molecules can be bound to these metal cations?

d) What is the nature of the cation-hydrogen interaction and their impacts on designing hydrogen storage materials?

e) Whether can these cations retain their affinity towards the hydrogen even in the presence of solid frameworks (host materials)?

In order to address the above issues, we have proposed some of the elegant chemical concepts for designing the materials for hydrogen storage:

1. Ion-Molecule interaction mediated hydrogen adsorption
b) Aromaticity induced hydrogen adsorption
c) Nanoscale curvature induced hydrogen adsorption

Apart from the above problems, another major issue is with the selection of theoretical methods. Since the interaction of molecular hydrogen with any surface is very weak, theories should be able to handle the type of interaction from dispersion, van der Waals to dipole-induced interactions. It may be noted that such type of interactions and the associated energies fall roughly within the range of correlation energy and hence, higher level of electronic structure methods including the electron correlations are very necessary. Most of the conventional theories and methods with model potentials can fail and lead to erroneous results. Keeping these conditions as a cautionary warning in our mind, we have applied both the \textit{ab initio} and DFT based methods for exploring the materials for hydrogen storage.

First, we made an attempt to understand the molecular hydrogen adsorption with the s-block metal cations (alkali and alkaline earth metal cations), as they are lighter elements compared to the transition metals. Herein, the proposed mechanism is through the electrostatically driven ion-molecular interaction of dihydrogen with s-block metal cations. Our results demonstrate that the number of hydrogen molecules attached to the metal cation is the highest (M+(H2)8, M=Na, K) even reported in the literature and the interaction strength between s-block metal ions with hydrogen is also found to be suitable for designing the materials for the hydrogen storage (Figure 1A). The calculated binding energy for hydrogen molecular interaction (MP2 method using cc-pVDZ basis set) is observed to be of the order of -30 to -13.5 kcal/mol for the case of alkali metal cations. Interaction of molecular hydrogen with anions, especially the halide ions (F-, Cl- and Br-) have also been carried out and our results reveal that (i) the halide ion-H2 bonds are linear but not T shaped (as shown in Figure 1A) as in the case of metal cation-H2 complex and (ii) for the case of chloride ion complex case, maximum of 12 hydrogen molecules are adsorbed in a highly symmetric manner with an icosahedral geometry in the 1st solvation sphere. The interaction energy of hydrogen molecule with chloride ion is observed to be in the range of - 2.2 kcal/mol per hydrogen molecule. Using this simple ion-molecule interaction, the possibility of the application of these complexes for developing hydrogen storage materials has been made through the carbon nanomaterials, specifically the fullerene based materials. These nanomaterials otherwise are very neutral and the hydrogen adsorption is observed to be very weak. Later, we demonstrated that doping of alkali metal atoms into fullerenes causes a remarkable enhancement in the hydrogen adsorption capacity. For instance, if eight sodium atoms are doped with C60 fullerene, the total number of adsorbed hydrogen molecule is found to be 48, with a gravimetric density of ~ 9.5 wt %. The adsorption efficiency of the proposed fullerene based material is observed to be better than other types of complexes particularly with the transition metal atoms.

We further extended the concept ion-molecule interaction for other types of carbon nanomaterials. Our results led to an important conceptual proposal on the curvature of nanosurface. The reactivity of the carbon nanomaterials can be enhanced remarkably not only by the electrostatic forces but also by tuning different types of curvature into the carbon nanosurface. The concept of curvature is basically understood from the structural parameters of the carbon nanosurface (as shown in Figure 1B) and it can be also used as one of the descriptors to assess the reactivity pattern of the carbon nanomaterials, including the nanotubes and fullerenes. Herein, we have observed that if we move from a planner benzene type of systems to a curved pattern of carbon hexagonal rings, the binding strength of sodium atom increases drastically with the curvature: 0.5 to -21.3 kcal/mol and there is a spontaneous (gradual) ionization of the sodium atom upon binding with the curved benzene structure. The charge acquired by the sodium atom (+0.6au) due to the effect of curvature in benzene molecule is approximately comparable to that of sodium cation (+0.8au) interacting with the benzene molecule. The high reactivity of the curved carbon surface is related to the weakening of pi-pi bonds between the carbon atoms due to the bending of the carbon hexagonal ring which makes the system to have quasi-sp\(^2\)-sp\(^3\) hybridization with substantial s-orbital character.
One of the main issues with the transition metal ions is the clustering of these metal ions around the material surface due to the high cohesive energy. Due to this effect, individual ion-hydrogen molecular interaction is drastically reduced which directly affects the hydrogen adsorption gravimetric density. In view of this, we also made an attempt to investigate whether the s-block metal elements can cluster on top of the fullerene or not. It can be seen from Figure 1 that the carbon surface with individual metal atoms is better stabilized than that of cluster of metal atoms. For the case of sodium atoms interacting with C₆₀ system, the calculated energy difference between the cluster and individual atoms is in the range of ~10 kcal/mol. Thus, our results further validate on the suitability of the s-block doped materials for hydrogen storage.

Let us now move on to another concept, namely aromaticity and explain how this concept can be useful for designing hydrogen storage materials through the use of organic molecular systems CₙHₙ [n=4–6 and 8]. The 5m-carbon ring C₅H₅ has five electrons in the ring which falls short of one electron in order to become six electron containing aromatic system, satisfying the Hückel (4n+2) rule. When sodium atom is brought near to the C₅H₅ ring, it has been seen that a positive charge is created on sodium atom, indicating the possibility of complete electron transfer to the carbon ring from sodium atom. The ionized sodium atom thus can interact with the...

Fig.1:  
(A) Hydrogen adsorption with cation, anion and cation doped C₆₀ 
(B) Concept of curvature and a model system with 6m-carbon ring 
(C) Effect of clustering of sodium atoms around C₃₆ fullerene
hydrogen molecules very effectively, as observed in case of fullerenes and our results demonstrate that maximum of 6 hydrogen molecules can be added effectively with the C₅H₅-Na, with the interaction energy in the range of ~1.7 kcal/mol per hydrogen molecule. Since the benzene molecule is already a stable aromatic compound, there is no significant interaction between the C₆H₆ ring and sodium atom. Similarly, we also extended this concept to other carbon rings and observed similar hydrogen adsorption pattern. Further, we have also made an attempt to realize hydrogen adsorption efficiency of such molecular systems by converting into molecular materials through a self-assembled pattern by suitable modifications or substituents without affecting the aromaticity of the carbon rings. Accordingly, we designed a C₅ unit as a suitable ligand for the C₅H₅ ring such a way that they form a bridge between several C₅H₅ rings. Our results for the interaction of sodium at each site of (C₅H₅-C₅)₁₀ show that the interaction pattern remains the same and the charged surface is created. The subsequent hydrogen adsorption is also surprisingly comparable to the case of C₅H₅-Na without losing any of their characteristic property of the molecular complex, as shown in Figure 2.

After we proposed several materials for hydrogen storage, as mentioned above, few experiments have also been carried out on some of the selected materials, especially the alkali metal doped fullerenes and nanotubes.¹⁴,¹⁵ One of experimental results show that a lithium-doped fullerene (Li:C₆₀ mole ratio of 6:1) can reversibly desorb up to 5 wt % H₂ with an onset temperature of ~270 °C under optimized conditions. The range of temperature is significantly less than the desorption temperature of hydrogenated fullerenes (C₆₀Hₓ) and pure lithium hydride (decomposition temperature 500–600 and 670 °C respectively). In addition, it has also noted that the fullerene cage is found to be very stable which is slightly modified during multiple hydrogen desorption/absorption cycles. In another related experiment, the hydrogen adsorption efficiency was evaluated for the sodium intercalated (NaₓC₆₀) and it was observed that up to 3.5 mass% hydrogen can reversibly be absorbed in NaₓC₆₀ at 200 °C and a hydrogen pressure of 200 bar. Here also, it has been seen that the fullerene cages even with the high hydrogen loadings, the NaₓC₆₀ sample stays intact.

Fig. 2: Hydrogen adsorption in a self-assembled model complex: Alkali metal doped (Na-C₅H₅-C₅)₁₀ units:

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"Molecules to Materials"
Concluding Remarks

In conclusion, it is quite evident that there is a close match between the predictions made by the theoretical and experimental methods towards the design of materials for hydrogen storage. More importantly, the simple concept of ion-molecule based electrostatic interactions satisfies some of the important requirements for the hydrogen storage materials, (a) weak interaction (b) significant number of hydrogen molecules at the ionic site (c) light-weight materials through the usage of s-block elements. These proposed materials can stimulate further research in this area; particularly in designing new materials by exploiting the electrostatics mediated ion-molecular interactions.

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