A brief account of the theoretical observations made in the month of July, 20-25th, 2009, on particles contained in structures of ammonia borane; and on the general existence of hydrogen clathrates of ammonia borane¹

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Group Name: "The [z]Wasatch Trail"

One of the greatest challenges facing science today is to find a replacement for fossil fuels. One idea is that of the hydrogen economy, in which hydrogen is used as a mobile source of energy, much as gasoline is today. Hydrogen has the advantages that it is usually generated from water, and that its reaction with oxygen produces only water and energy. However, it suffers from two major problems: the production of hydrogen from water uses more energy than it generates, and hydrogen is a difficult material to transport. We focus on the second of these problems, where clathrates of the molecule ammonia borane may have promise as a storage medium giving both high density of hydrogen and relatively easy access to the caged molecular hydrogen.

We are approaching this problem from several angles simultaneously. There are essentially three branches, which we will use to check the consistency of our methods. The first branch is a semianalytical model to predict PT-stability. The second branch will use the DFT methods coded in the VASP program to calculate the phonon density of states and therefore the free energies. The third branch will develop a potential energy surface for the ammonia borane clathrate interacting with molecular hydrogen, which will then be used for computational studies of statistical mechanical and dynamical properties. Brief descriptions of each of these branches are contained in the following pages.

From these studies, we hope to determine whether the ammonia borane clathrate has potential as a material for hydrogen storage. If it does, we save the world, get rich, and so forth.

¹ With apologies to Robert Brown. Of course, he probably doesn't care, since at this point he has "reached equilibrium."

Picture: Hydrogen Report Switzerland 08/09

As a possible solution to environmental and energy problems hydrogen economy remains unrealized due to following main reasons: (i) hydrogen production and (ii) hydrogen storage.



Hydrogen storage

Accessibility

Chemical compounds	NH ₃ ; Mg(NH ₃) ₆ Cl ₂ ; NH ₃ BH ₃	Density
Chemisorption	Metal hydrides: LiAlH ₄ ; NaBH ₄ ; Al(BH ₄) ₃	
Physisorption	High surface area materials: MOFs; carbon based materials	
Liquefaction	20 K	
Compression	200-700 bar	

Problem of storage may be solved by designing hydrogen content material and enclosed guest clathrates in which host material is a high molecules are molecular hydrogen

Clathrates of ammonia borane



- Analogy to Bernal-Fowler rules allows one to identify possible frameworks
- are used to refine structures and Electronic structure calculations estimate strength of host-guest interactions
- Practical questions remain:
- What is PT stability zone?
- How does stoichiometry depend upon PT?

Model

 Let us consider free energy change for process of enclathration



$$= E_{HCG} - T(S_{ST} - S_{PSB}) = 0$$

- the interaction energy between host cage and guest molecule; T
 - the Sackur-Tetrode entropy of ideal gas;
- the entropy of a particle in a spherically symmetric rectangular potential well (the entropy of a particle in a spherical box).

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DFT Calculations

From:

B. G. Janesko, T. M. Henderson, and G. E. Scuseria, *Cond. Mat.*, arXiv0901.3935 (2009)

- Computing the interaction energy between $H_3B \cdots NH_3$ and H_2 requires high accuracy methods.
- Coupled-Cluster theory would be suitable, but has a very bad scaling behaviour (N⁶/N⁷) considering that more than hundred singlepoint calculations are needed.
- MP2 would be more feasible.
- All correlated wavefunction methods require very large basis sets (at least cc-pVTZ or even larger) to obtain reliable high accuracy results.
- Range-separated DFT with a different treatment of short-range and long-range interactions

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \underbrace{\frac{\operatorname{erfc}(\omega|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}}_{\operatorname{SR}} + \underbrace{\frac{\operatorname{erf}(\omega|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}}_{\operatorname{LR}}$$

is a promissing approach to obtain high accuracy and computational efficiency. Therefore,

$$E_{\rm XC} = E_{\rm X}^{\rm SR, \ \rm DFA} + E_{\rm X}^{\rm LR, \ \rm HF} + E_{\rm C}^{\rm SR, \ \rm DFA} + E_{\rm C}^{\rm LR, \ \rm dRPA}$$

will be used.

- Less basis set dependent.
- Smaller BSSE. Anyway, the BSSE will be corrected using the Counterpoise method.
- High accuracy interaction energies can be expected.

Developing a Potential Energy Surface, and using it for semiclassical dynamics

David W.H. Swenson

Making a Potential Energy Surface in the MMC Framework

- 1. I'll get the dimer and electrical *ab initio* energies from Robin in order to make the potential energy surface
- 2. There are many ways to make a PES, we choose the form of Molecular Mechanics for Clusters (MMC) [1] ... mainly because I'm familiar with it
- 3. MMC:
 - is a rigid monomer potential
 - uses an accurate treatment of the electrical properties of the molecule combined with a dispersion correction (usually 6-12 interactions)
 - site based for the dispersion interactions, with on the order of twice as many sites as atoms
- 4. Practical issues:
 - H₂ has already been done, [2] so we just have to fit the host for the host-host and host-guest interactions
 - The host-host interaction will probably be dominated by the electrical interactions, so (we hope) we can focus on the host-guest system for fitting the dispersion interactions
 - Previous example: H₂-benzene was fit to an RMSD of 15.7 cm⁻¹ [3]

Using the PES for Semiclassical Calculations

- 1. Use the PES for dynamics why semiclassical instead of classical?
 - weakly bound complexes tend to be very anharmonic
 - zero point energy is significant in weakly bound complexes: ZPE eats up 2/3 of the H₂benzene global minimum [3]
 - hydrogen is light, so there may be interesting quantum dynamical results (depends on shape of PES)
- 2. Method to use: LSC-IVR [4]
 - simple method (not much harder than classical mechanics) which works on large systems
 - Any time correlation function: flux-side for rate and kinetic isotope effect (after finding a dividing surface), position autocorrelation for spectrum, etc.

References:

[1] C. E. Dykstra. *J. Am. Chem. Soc.* **111**, 6168 (1989).

- [2] M. Carmichael, K. Chenoweth, and C. E. Dykstra, J. Phys. Chem. A 108, 3143 (2004).
- [3] D. W. H. Swenson, H. M. Jaeger, and C. E. Dykstra. Chem. Phys. 326, 329 (2006).
- [4] H. Wang, X. Sun, W. H. Miller. J. Chem. Phys. 108, 9726 (1998).

Computer simulation of Ammonia-Borane Clathrate of Hydrogen

Avisek Das

July 25, 2009

Classical statistical mechanics based computer simulations will be performed on the material to understand structure of the clathrate at nonzero temperature and amount of hydrogen captured at various temperature and pressure. We will use structure and empirical potential energy functions calculated by collaborators (Alexander Abramov, David Swenson, Robin Haunschild, Yumei Zhang, Jiawei Xu).

1 Grand Canonical Monte Carlo Simulation

In order to understand how the efficiency of hydrogen capture changes with temperature (T) and pressure (p) we propose to perform Grand Canonical Monte Carlo simulation at constant pressure, temperature and constant chemical potential. This simulation will sample the μPT ensemble. The constant pressure in this case is the hydrostatic pressure of the hydrogen gas.

Our starting structure will be an unit cell of the clathrate with some or all the hydrogen molecules present in the cavities. We can also have more than one unit cell in the simulation cell if we need better statistics. Various initial conditions will be tried to check for proper equilibration of the system. Periodic boundary conditions will be used in all three dimensions. Simulations without PBC will also be performed to understand the effect of small cluster but those may suffer from severe system size effects. We will calculate the chemical potential of the hydrogen gas by using standard technique. Monte Carlo moves will consist of following different kind of moves

• Insertion of a hydrogen molecule. The move is accepted with a probability of

$$p_i = \left(2\pi m k_B T / h^2\right)^{3/2} \left(V / (N_g + 1)\right) \exp\left(\left(\mu' - w\right) / k_B T\right)$$

where N_g is the number of hydrogen molecule, μ' is the chemical potential of hydrogen and w is the interaction potential of new hydrogen with all the other molecules.

• Deletion of a hydrogen molecule. The move is accepted with probability

$$p_d = \left(2\pi m k_B T / h^2\right)^{-3/2} \left(N_g / V\right) \exp\left(\left(-\mu' + w'\right) / k_B T\right)$$

where w' is the interaction energy of the chosen guest with all other molecules.

- Move particles in the simulation cell. Move is accepted using standard Metropolis criterion.
- Change the volume according to regular constant pressure (NPT) Monte Carlo.

After an equilibration for certain number of steps we do a production run and calculate the average number of hydrogen molecule captured in the clathrate. We can also look at how many hydrogen molecules are encapsulated in one cavity. This calculation can also give us some idea about the effect of finite temperature and pressure on the structure of the compound in presence of guest molecules.

If we repeat this calculation for several temperatures and pressures we can get an idea about the efficiency of hydrogen storage as a function of temperature and pressure.

Da plan¹

	0	12mth	24mth	36mth
Da model ¹				
Phonon DOS				
Electronic Structure Calculations for PES				
Fitting PES, Testing				
StatMech on PES				
Semiclassical Dynamics				

¹With apologies to Da Bronx and/or Da Chicago Bears