

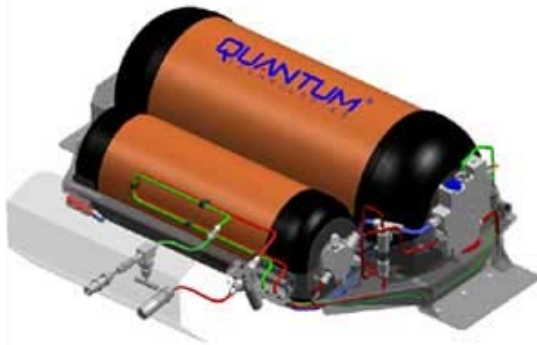
GECP Hydrogen Project:
"Nanomaterials Engineering for
Hydrogen Storage"

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Students and Staff Members:
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Experimental Collaboration:
H. Dai, B. Clemens, A. Nilsson

Hydrogen Storage Technologies



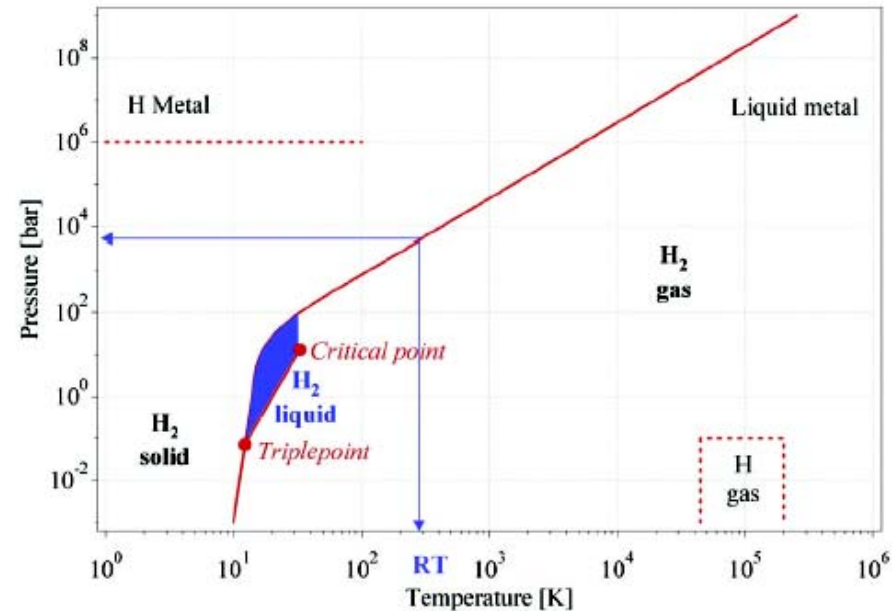
High pressure tanks

- 5,000-10,000 PSI (35-70 MPa)
- up to 12wt% H₂ (system)
- Compression energy losses (3 kWh/kg)
- Variable pressure delivery
- Safety issues
- Low volume density



Liquid cryogenic storage

- ~ 8 Wt% H₂ (system)
- Evaporative losses (0.4%/day)
- Cooling costs (15 kWh/kg)
- Safety issues



Pressure-Temperature diagram of hydrogen

Multiscale *Design* of Nanomaterials for Hydrogen Storage

Chemisorption: $\text{H}_2 + \text{NM} \rightarrow \text{NM-2H}$

- H-H bond breaking = 4.52 eV
 - poor reversibility (**too strong bonding**)
- + high surface coverage
- ? stability of NM-2H states

Physisorption: $\text{H}_2 + \text{NM} \rightarrow \text{NM-H}_2$

- + weak adsorption
 - good reversibility
- small surface coverage (**much less than a few wt. %**)

***Controlled Catalytic* Chemisorption**

- + high surface coverage & good reversibility

Rational Design of Hydrogen Storage Material

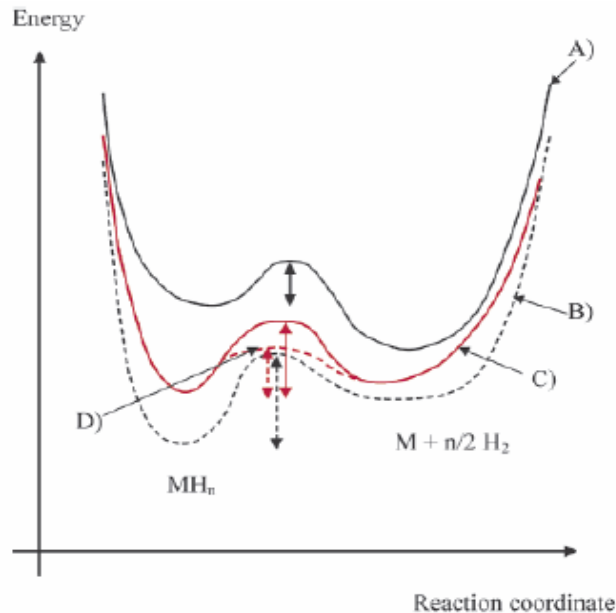
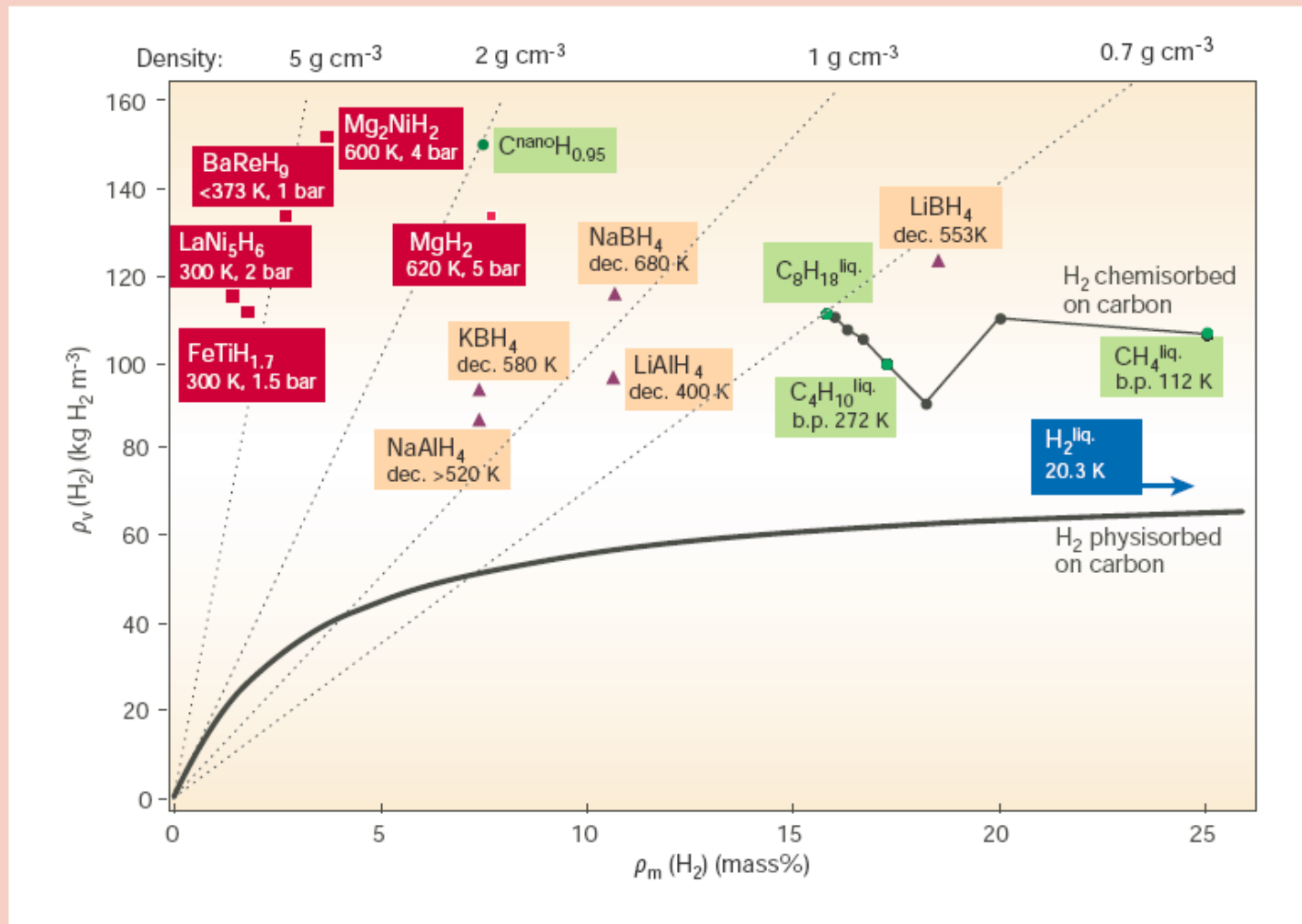


Figure 12. Reaction path for hydrogen evolving from different HSMs. (A) Thermodynamically very unstable HSM with low activation barrier and low T_{dec} , which stores hydrogen irreversibly. (B) Thermodynamically very stable HSM with high activation barrier and high T_{dec} , which stores hydrogen reversibly. (C) Thermodynamically slightly stable HSM with intermediate T_{dec} , which stores hydrogen irreversibly. (D) Target situation: catalytically enhanced thermodynamically slightly stable HSM with low T_{dec} , which stores hydrogen reversibly. Vertical arrows symbolize the activation barrier for the decomposition process.

- High Storage Capacity: 6.5 wt%, 65 g/L
- Desorption Temperature: 60~120 °C
- **Thermodynamically slightly stable** hydrogen storage systems are desired and can be achieved through material engineering.
- **Reversibility dilemma:** Reversibility is usually associated with high-energy barrier for dissociation and adsorption.
- **Solution: Engineered catalyst** can tune the energy barrier.

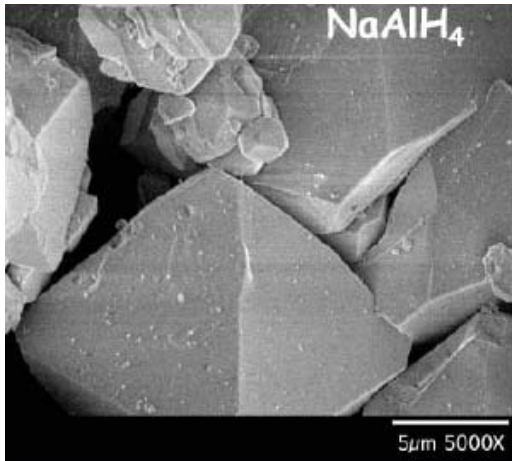
Hydrogen Storage Capacity of Diverse Materials

Figure 6 Stored hydrogen per mass and per volume. Comparison of metal hydrides, carbon nanotubes, petrol and other hydrocarbons.

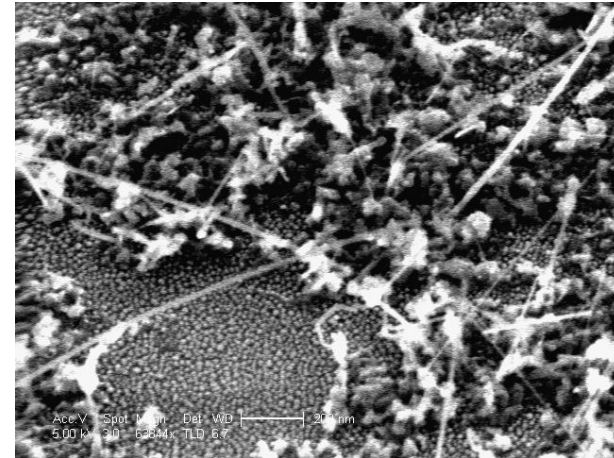


Candidate Nanostructures for Hydrogen Storage?

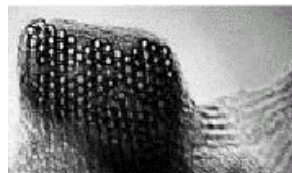
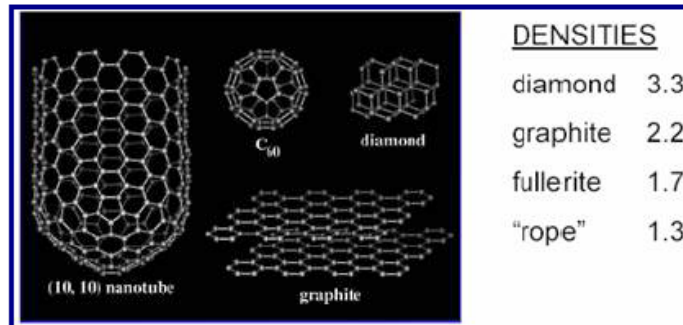
I. Metal Hydrides



III. Semiconducting Nanowires

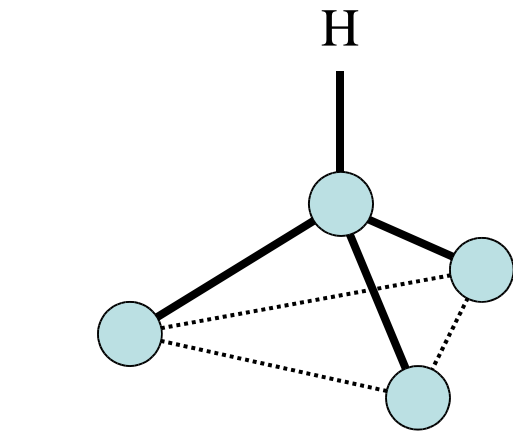
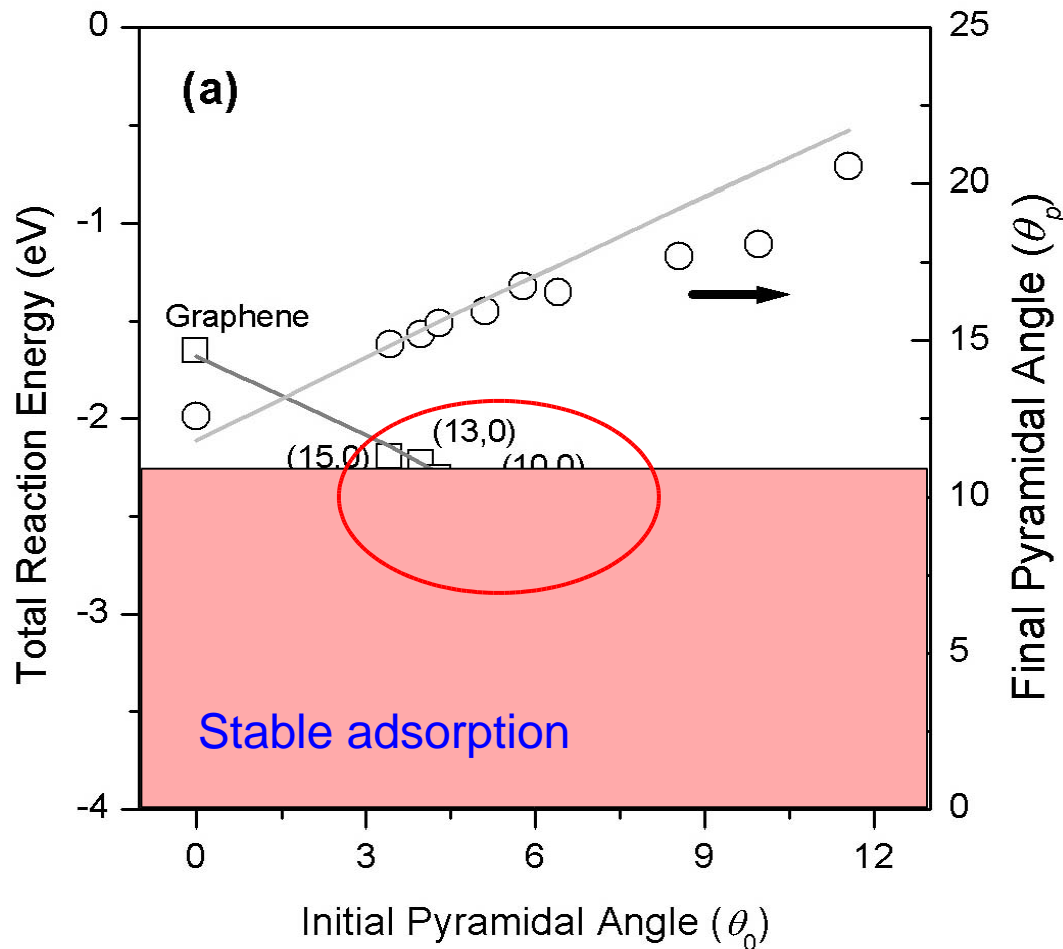


II. Carbon Nanotubes



TEM of a single walled nanotube, typical tube diameter is 1.4 nm, taken from <http://cnst.rice.edu>

Controlled Hydrogen Bonding on Carbon Nanotubes

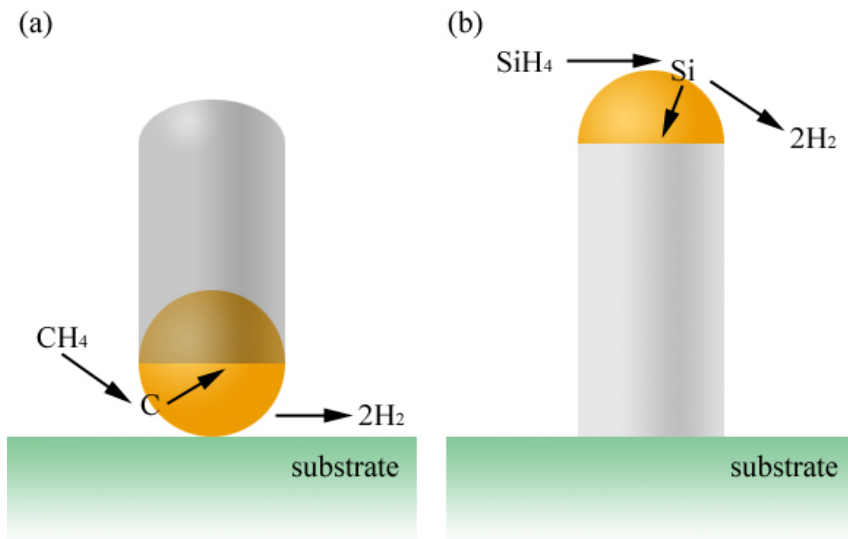


stability of chemisorbed hydrogen (NM-2H) states relative to H_2 gas can be tuned by nanotube size: **(8,0) - (12,0) CNTs** would have enough binding energy (**up to 0.5 eV**) per H_2 molecule

Prediction (solid curves)
Ab-initio results (□ and ○)

S. Park, D. Srivastava, and K. Cho, "Local reactivity of fullerenes and nano-device applications," Nanotechnology 12, 245 (2001).

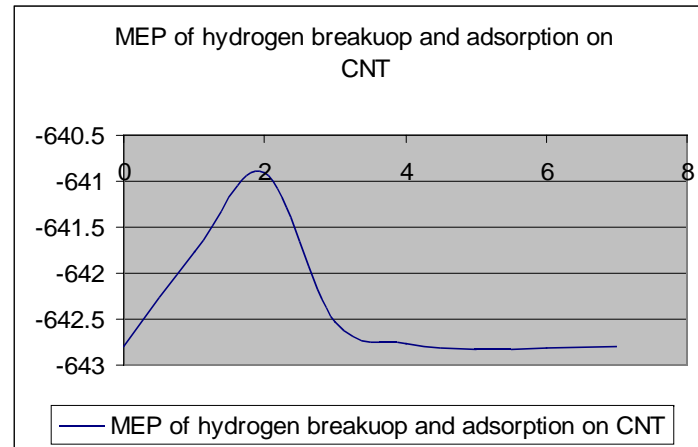
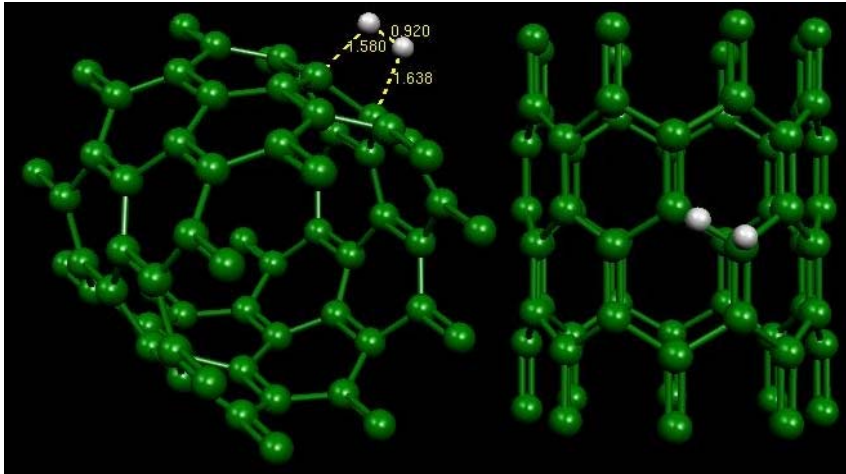
Controlling Nanotube Diameter by Rationally Designed Catalyst Nanoparticle.



(a) CNT growth from catalyst particles
(b) SiNW growth from catalyst particles

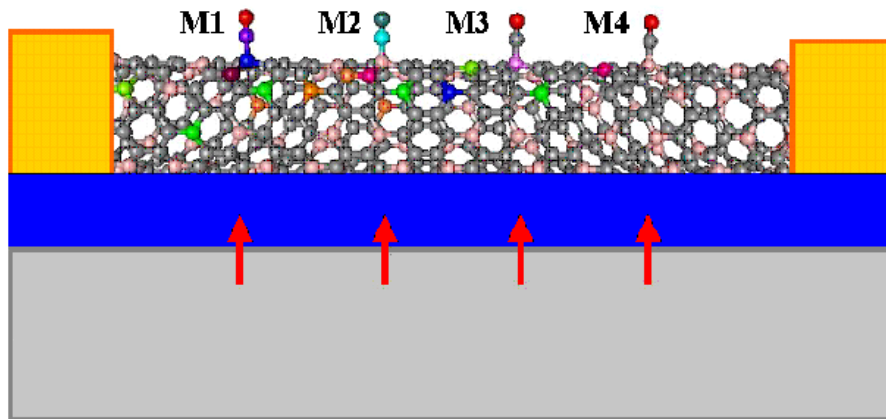
- Diameter (of CNT's and SiNW's) is correlated to the size of metal nanoparticles
- What determines the correlation?

DFT Calculation of Hydrogen Adsorption on CNT



On pure CNT, the barrier for dissociative adsorption of hydrogen is High

How to Reduce the H-H Bond Breaking Energy on Carbon Nanotubes?



Doped CNT to create stable catalytic sites for H-H dissociation

Metal atoms on CNT surface for controlled catalytic H-H dissociation →



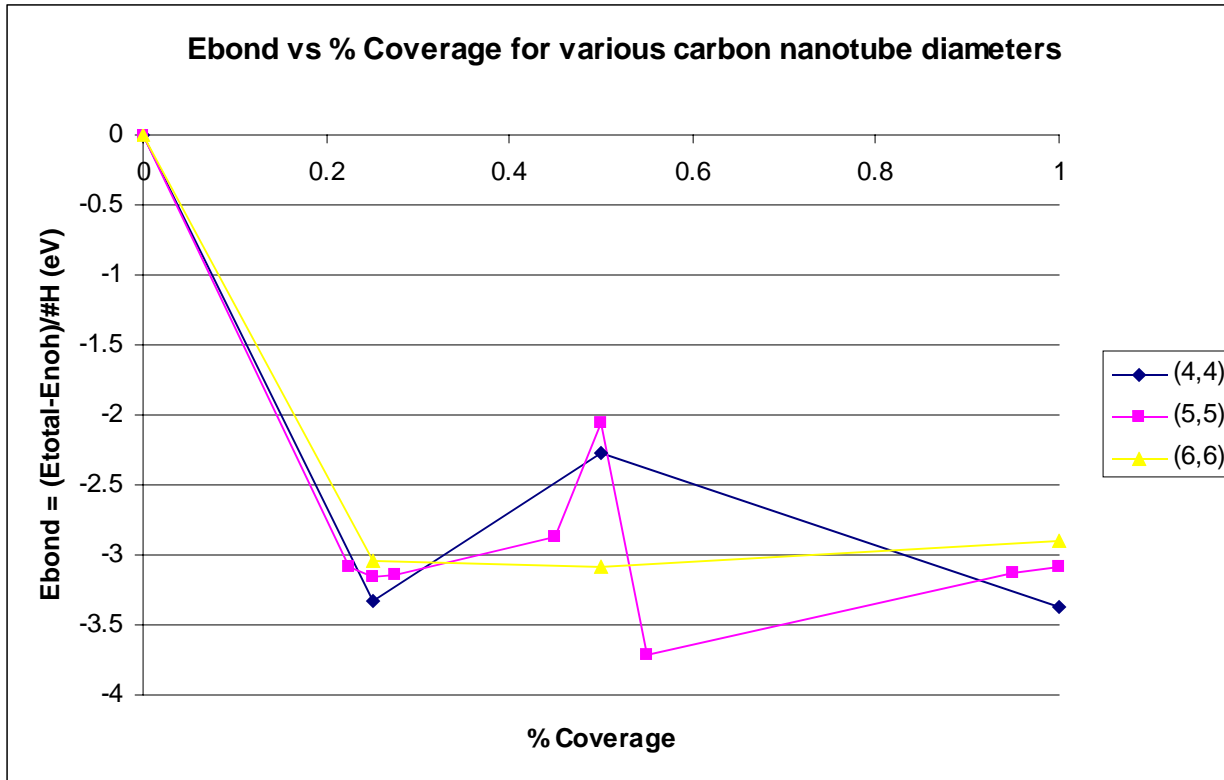
S. Peng and K. Cho, "Ab initio Study of Metal Atoms on SWNT Surface," MRS Symposium Proceedings Vo. 675, W4.8 (2001).

S. Peng and K. Cho, "Ab Initio Study of Doped Carbon Nanotube Sensors," *Nano Lett.* 3(4), 513-517 (2003).

Key Questions

- Which carbon sites does hydrogen attach to as the coverage increases (what is the distribution of H look like on the CNT surface)?
- What is the maximum hydrogen coverage?
- How does the maximum hydrogen coverage vary with different diameter nanotubes?

1st Attempt to Plot Energy vs % coverage for different Nanotube Diameters (DFT)

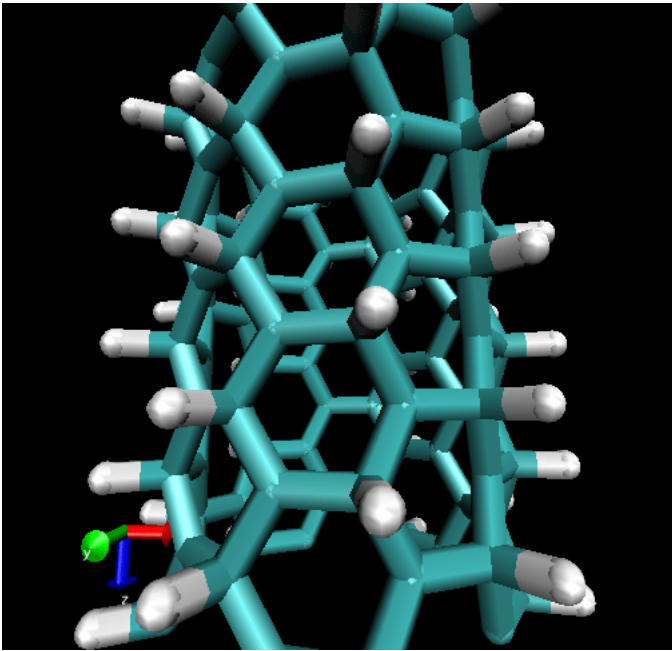


-previous results published at 100% coverage, confirmed

-lots of local minimums/interplay at lower coverages

-why the variation?

H Distribution Important

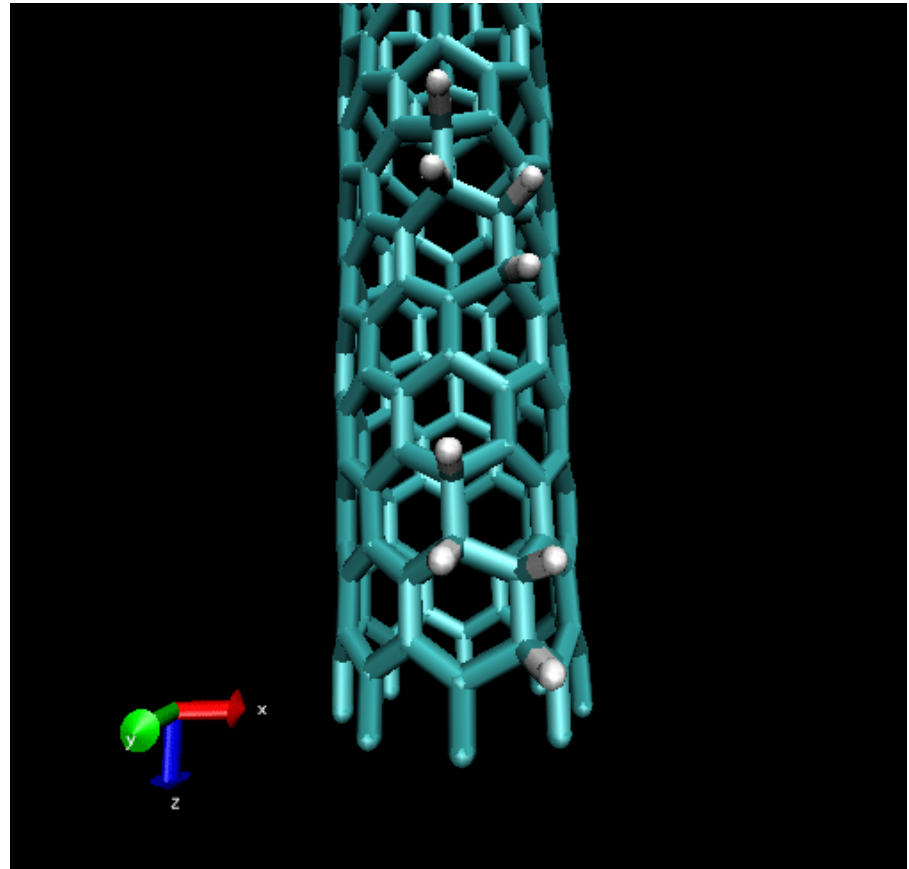
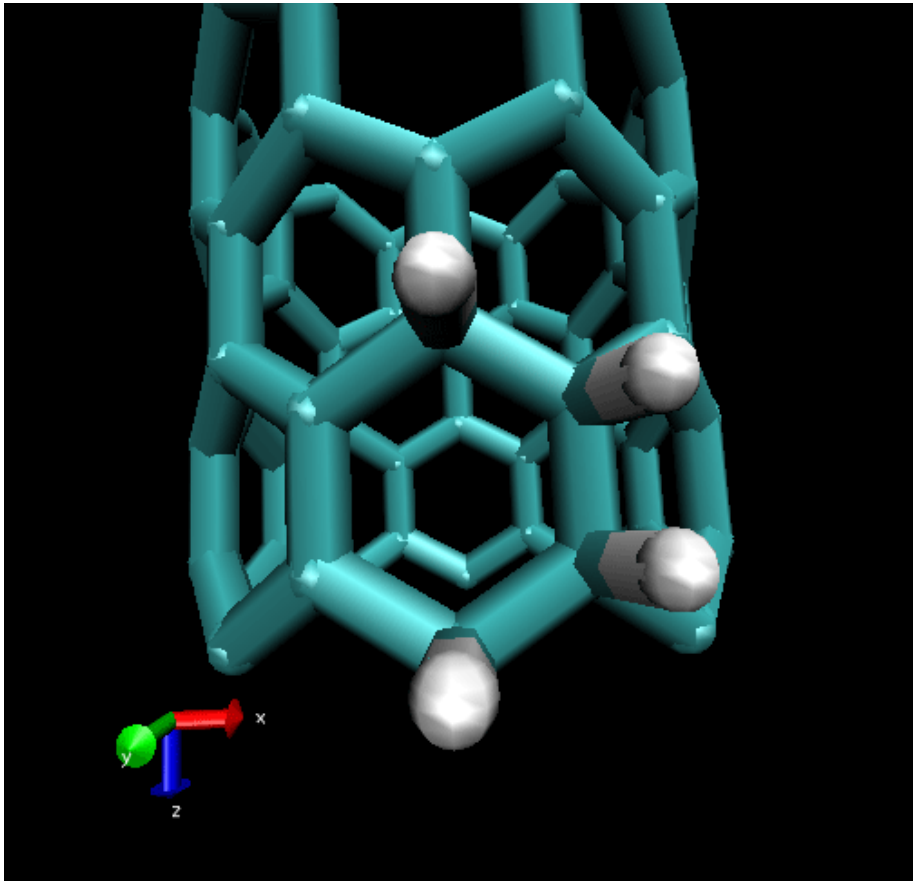


Unfavorable distribution of hydrogen

-hydrogen placement as well as % coverage play a vital role in determining stable energetics

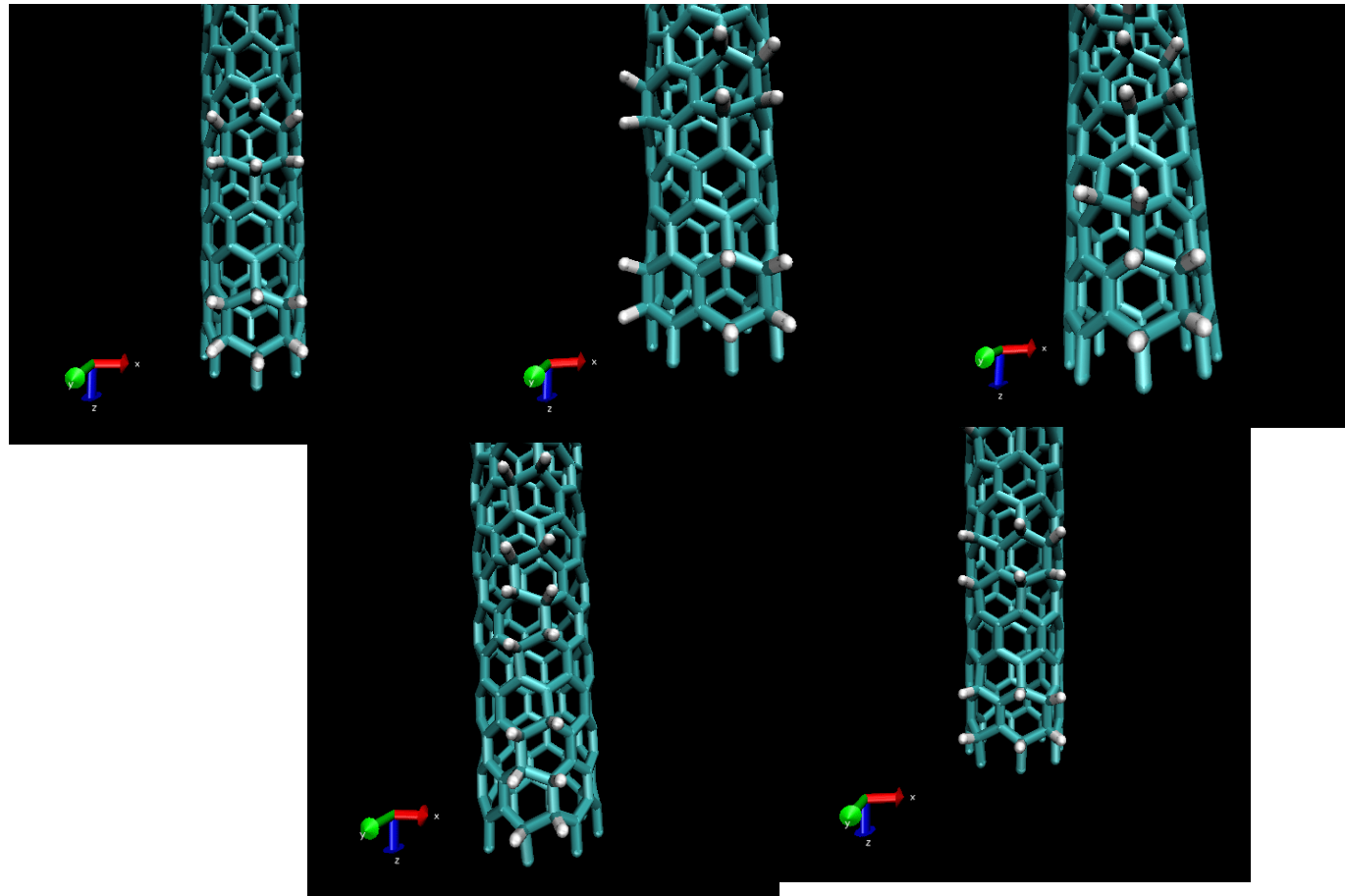
-need to find optimal/most probable distributions to compare

Optimal Distribution of 2 H Pairs



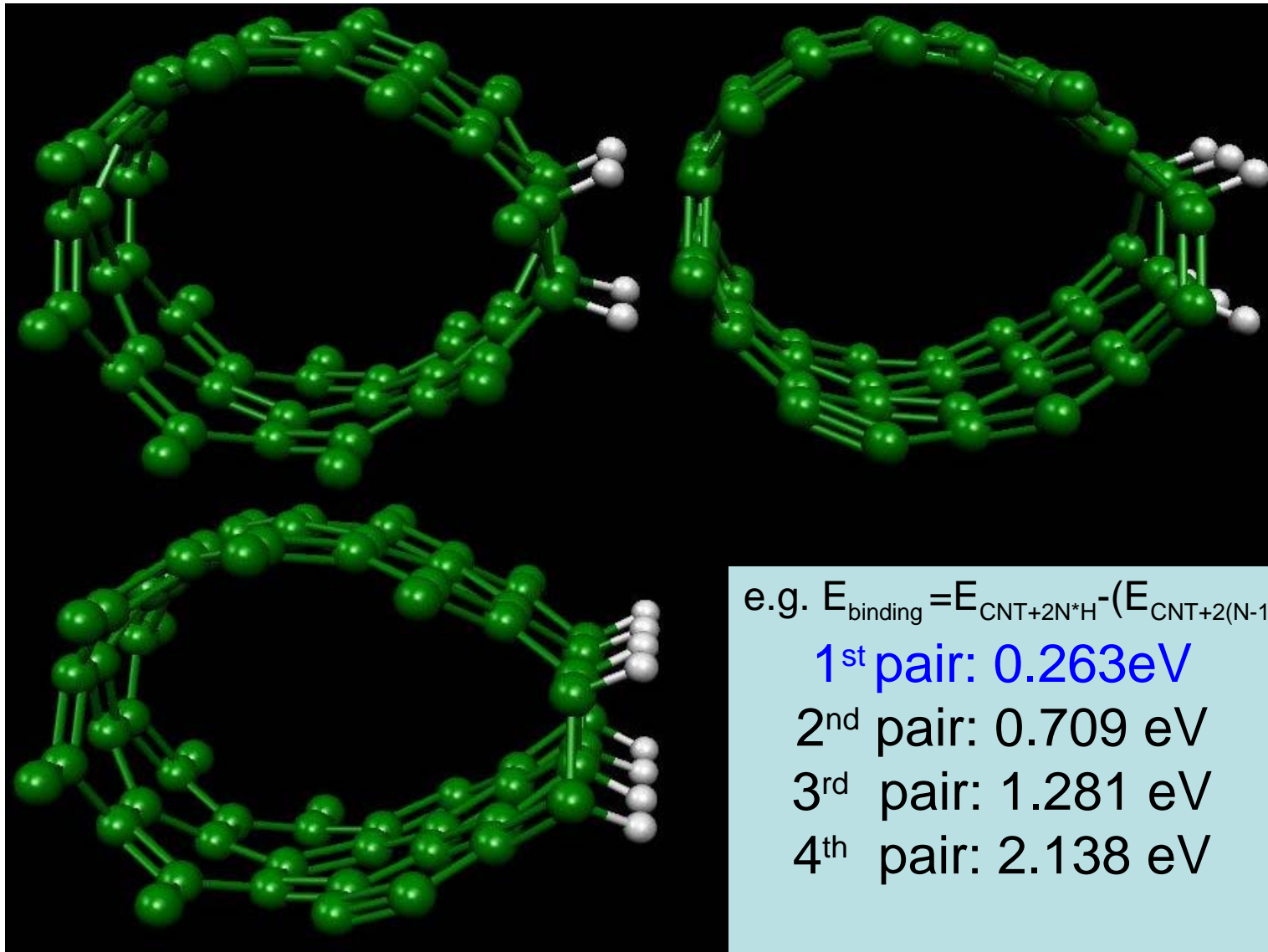
Two most favorable positions of 2 pairs of hydrogen

3 H Pairs Optimal Distributions

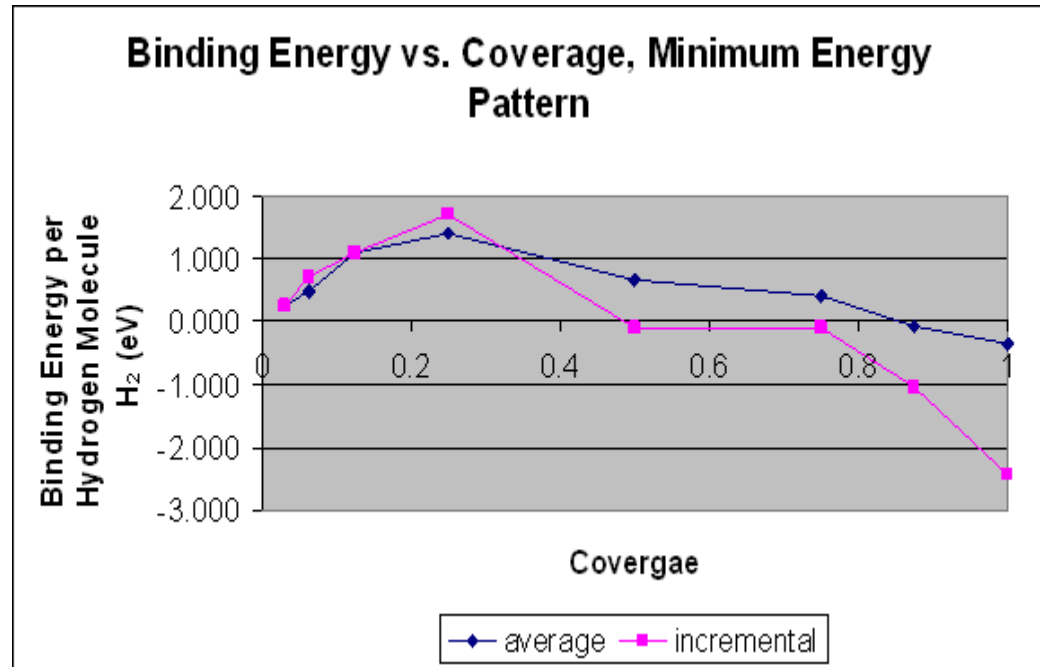
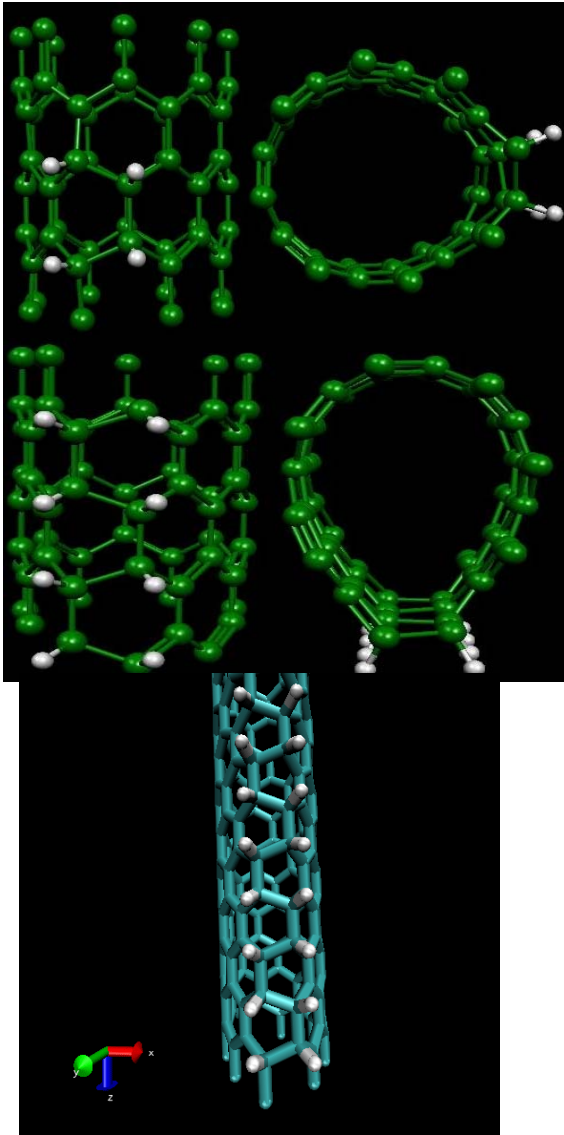


$E_{\text{bond}} = -3.55032\text{eV}, -3.50808, -3.48897, -3.44557, -3.43165$

Optimal Configurations of Adsorbed Hydrogen Pairs

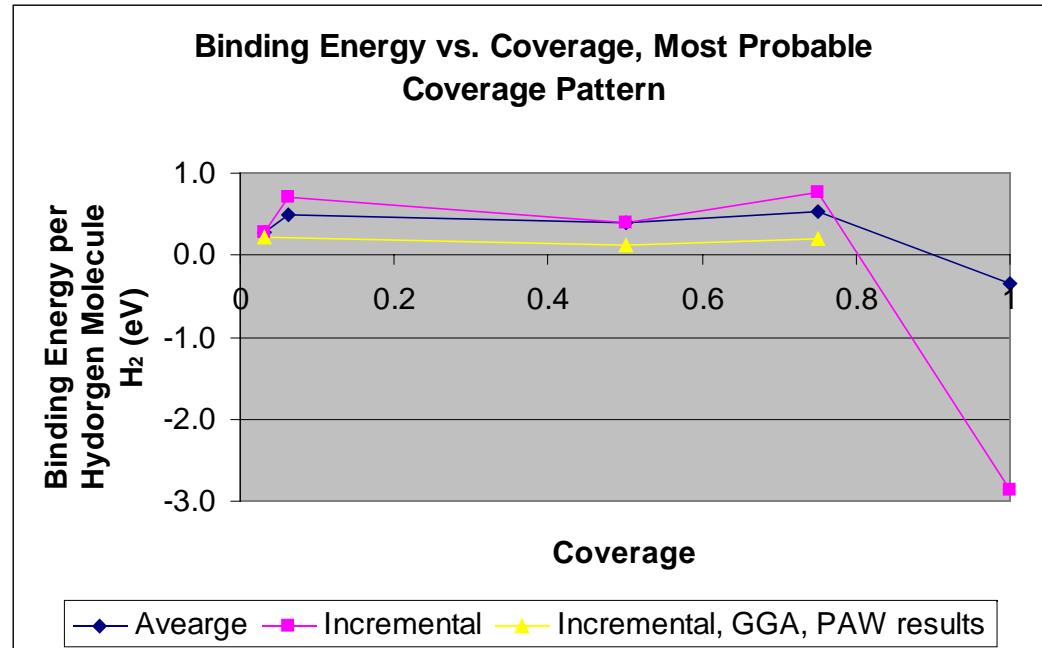
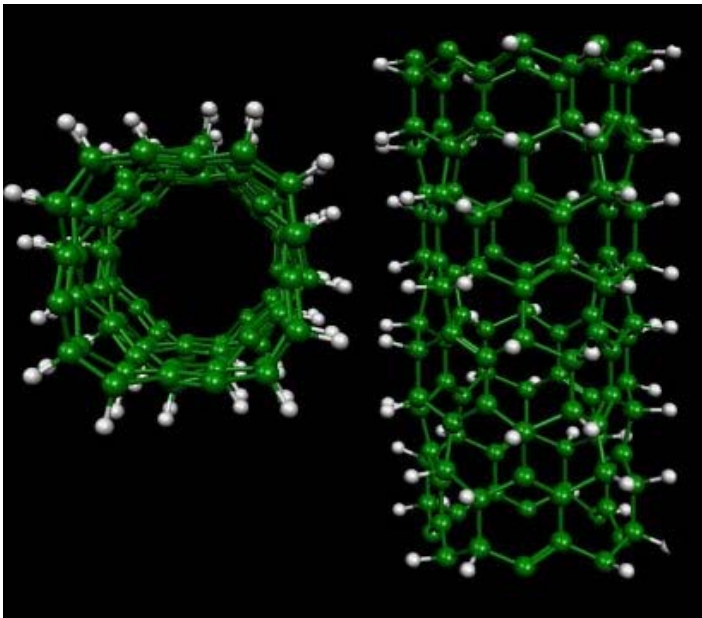
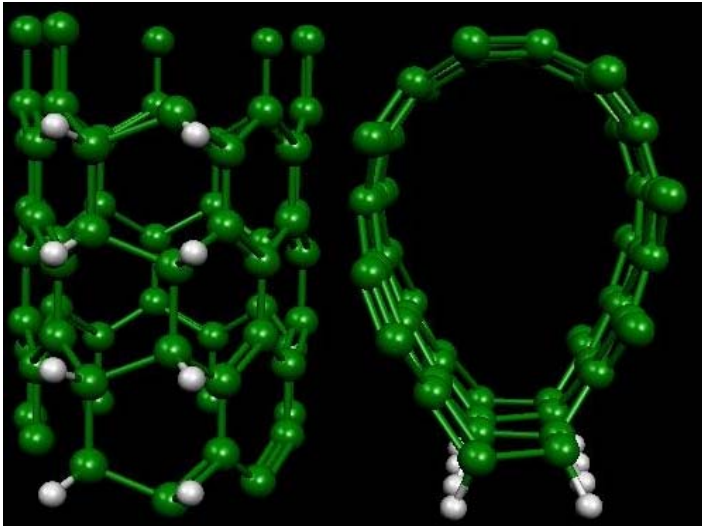


Coverage Dependence of Binding Energy (Stripes down Axial Direction)



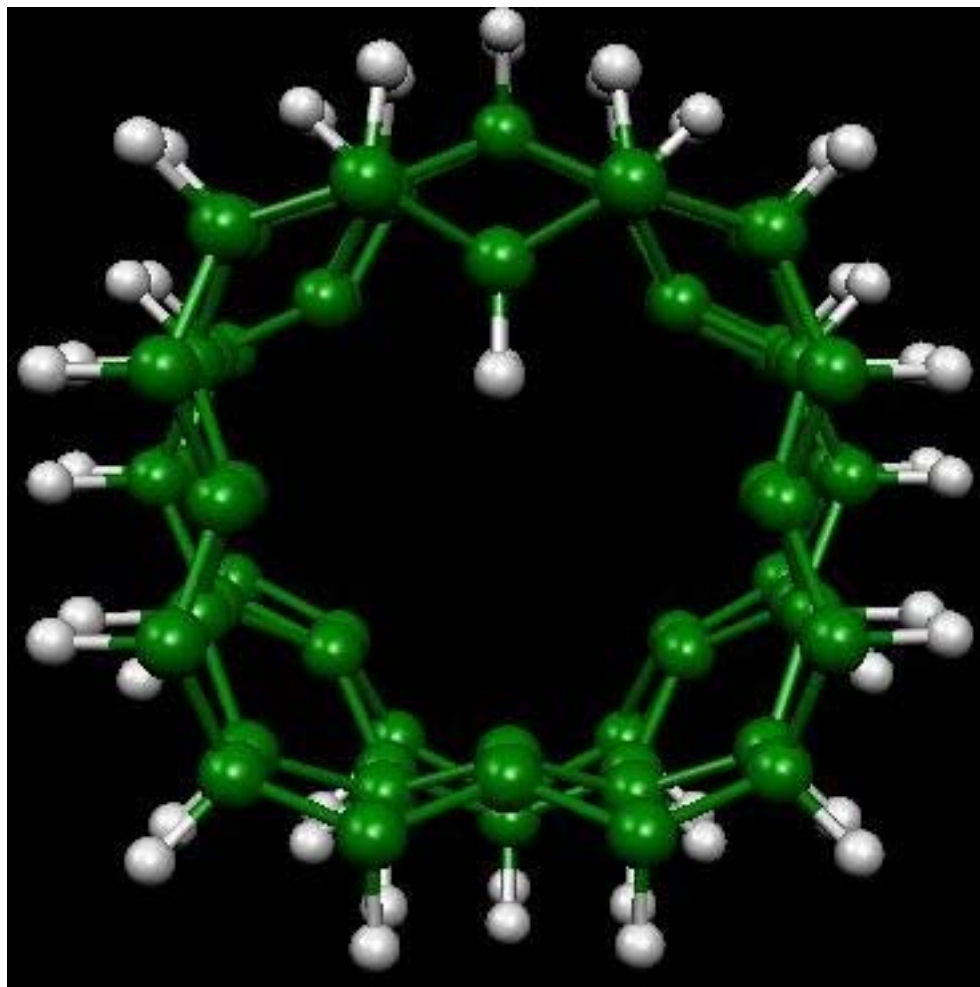
- The maximum chemi-sorption capacity is around 50% or less
- Binding is very strong at low coverage.

Coverage Dependence of Binding Energy (Even Distribution of Optimal 2 Pairs)



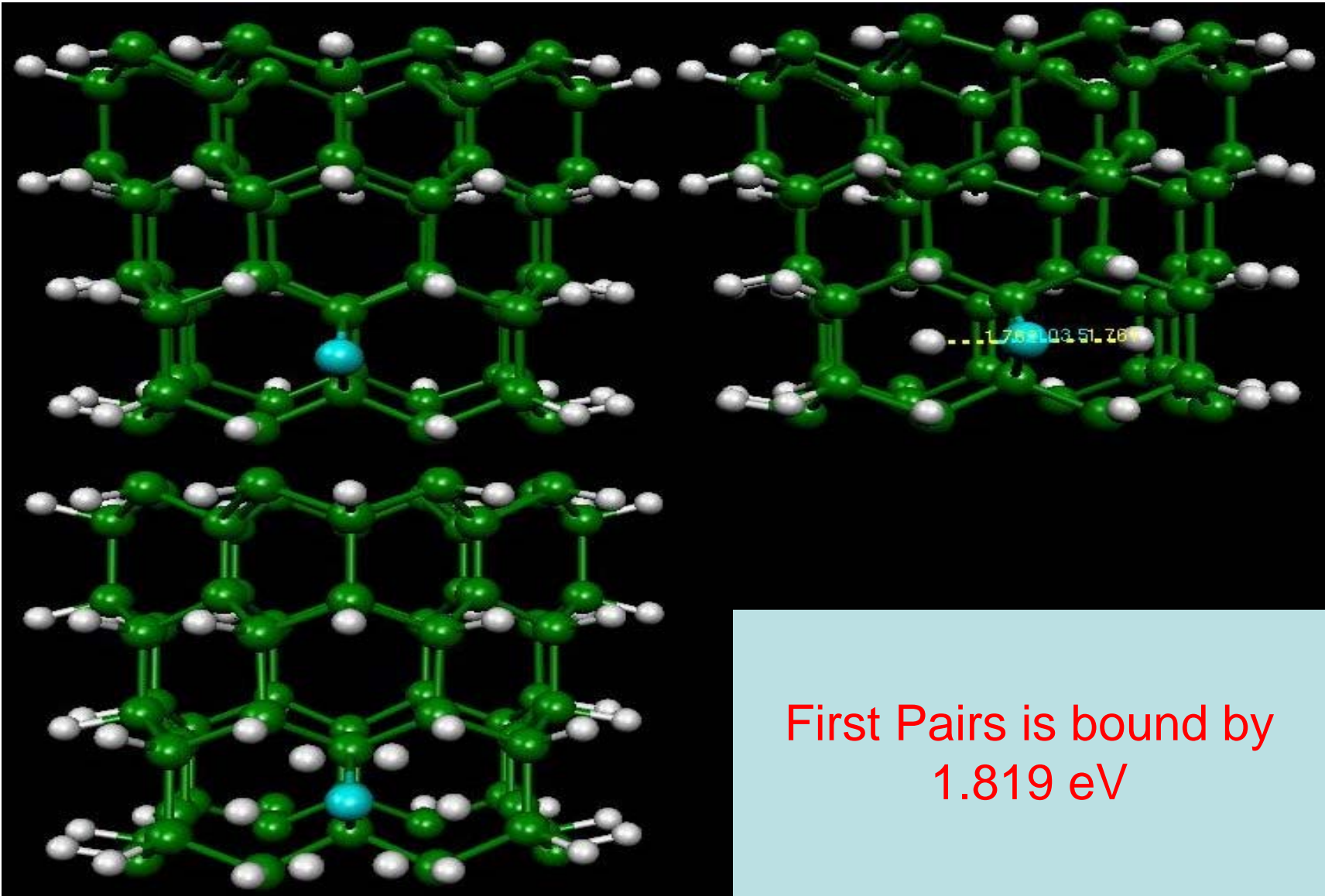
- The maximum coverage is around 75% with external binding.
- The binding energies are in a narrow range of 0.4 eV ~ 0.6 eV (0.12 ~ 0.22 for GGA and PAW)

At 75% Coverage, possible to start endohydrogenation

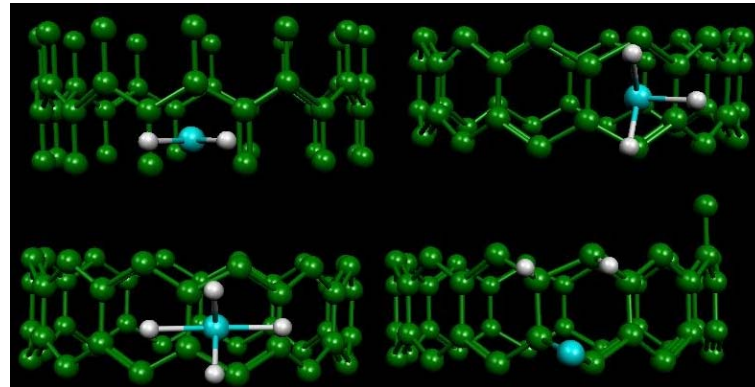
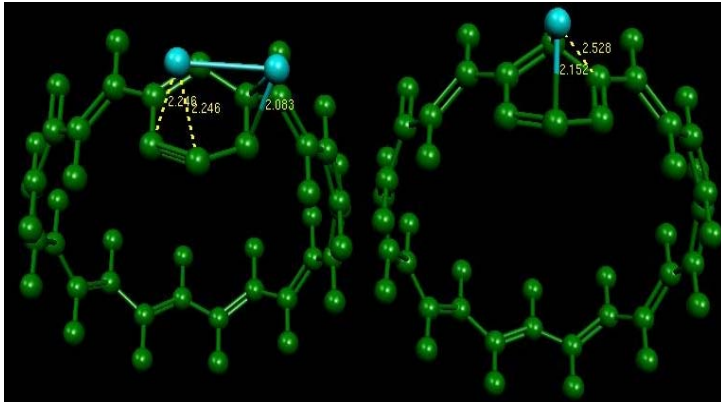


Binding Energy: 2.633 eV for addition pair!

Ti Metal Atom on CNT @ 75% coverage: How many H can bind to Ti?



Improving Adsorption/Desorption by Transition Metal Catalyst



Hydrogen Binding Configurations on Pt on CNT

- First pair of H₂ is strongly bound to Pt: 2.43 eV
- Second pair H₂ is slightly bound to Pt: 0.661 eV
- H₂ is bound to CNT stronger than the second pair of H₂ on Pt: 0.776 eV

Conclusions

- Hydrogen distribution on the CNT is a complex matter but changes the energy significantly at different sites
- Optimal 2, 3, and 4 pair configurations have been found
- Work still needed to understanding results

Multiscale Simulation Tools

1. Nanostructure generator, with electronic structure display from Tight-Binding calculation.
2. Multiscale modeling for nanoparticle design
 - Continuum modeling with bulk and surface energy.
 - MD atomistic modeling with XEAM, angle-dependent bond energy, and charge transfer.
 - Tight-binding and DFT for accurate electronic structure and reactivity.
3. Quantum Monte Carlo (QMC) for energetics with chemical accuracy.

Energetics with Chemical Accuracy from QMC

- Stochastic process based method for solving Schrodinger Equation
- Highly Efficient (Scales like N^3)
- Highly Accurate, approaching chemical accuracy of 1kcal/mol.

TABLE V. Comparison of methods.

Method	E_{corr}	$E_{\text{coh/bind}}$ % errors	Scaling with # of electrons	Total time for C_{10}
HF	0	$\approx 50\%$	N^3	14
LDA	N/A	15–25%	N^3 ^a	1
VMC	$\approx 85\%$	2–10%	$N^3 + \epsilon N^4$ ^b	16
DMC	$\approx 95\%$	1–4%	$N^3 + \epsilon N^4$ ^b	300
CCSD(T) ^c	$\approx 75\%$ ^d	10–15% ^d	N^7	1500 ^d

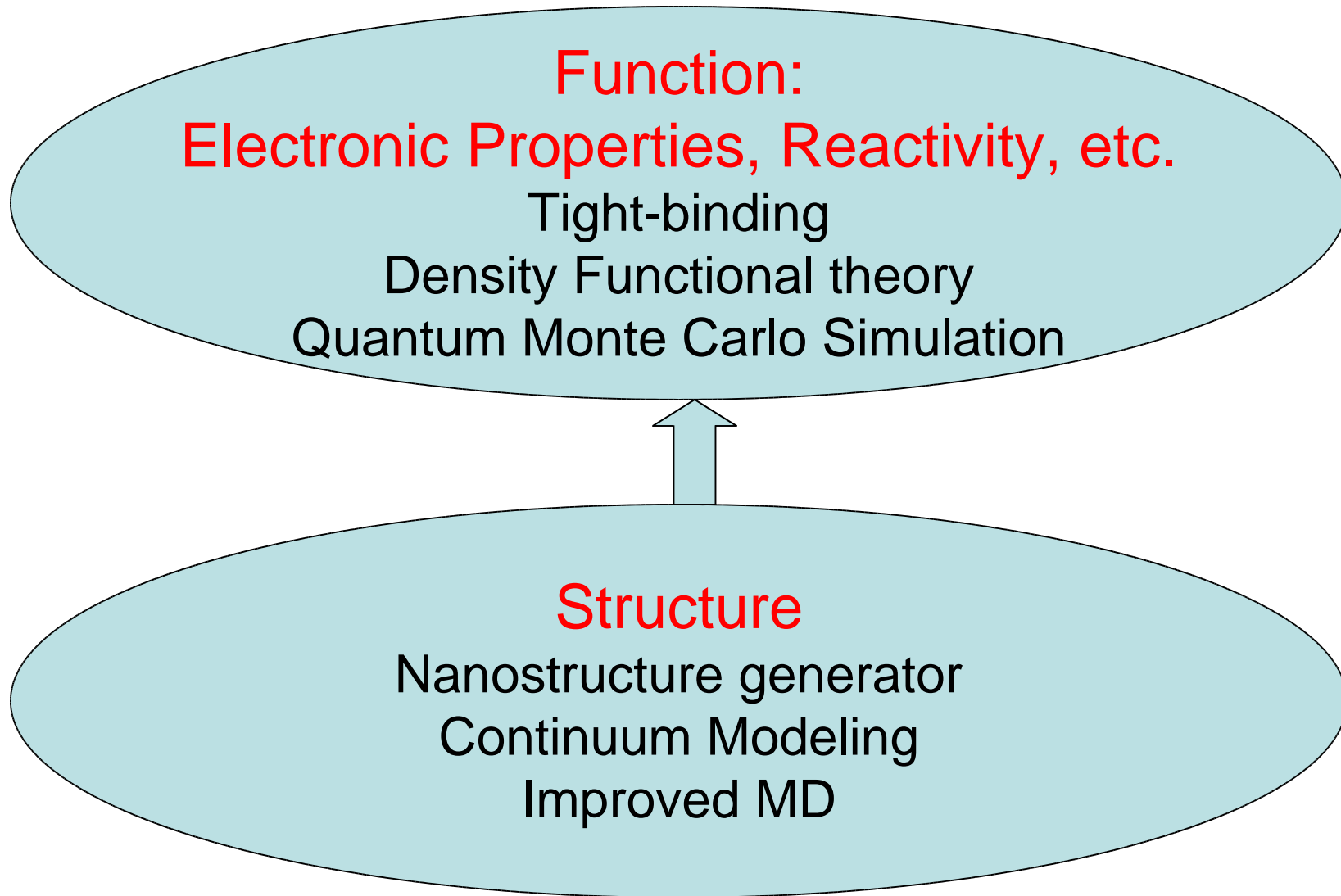
^aLDA algorithms with scaling proportional to N have been proposed.

^b $\epsilon \approx 10^{-4}$.

^cCoupled cluster with single and double substitutions, including triples noniteratively.

^dWith a 6-311G* basis set; in the limit of infinite basis set and order of excitations the coupled-cluster method is formally exact.

Nanomaterial Simulator

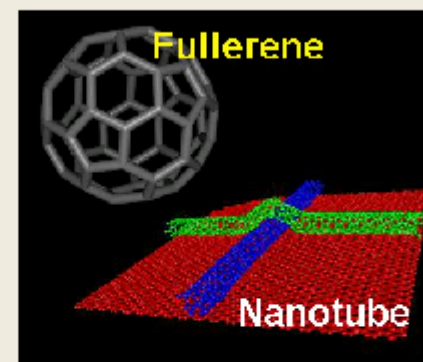
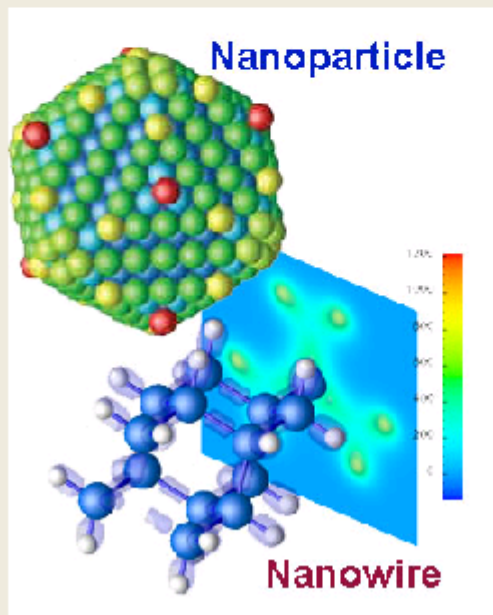


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[Nanoparticle](#)
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MSL Nanomaterials Simulator Version 1.1

Electronic Structure Module

MSL Nanomaterials Simulator is developed by Multi-Scale Simulation Laboratory at Stanford University. It provides an easy to use graphical user interface for designing and analyzing different nano materials including carbon nanotubes, nanowires, nano particles and any other user defined nano systems. Most of the tasks can be completed just by a few mouse clicks without preparing any format of input file. The user also has the control over what physical quantities to be calculated, such as density of states, bandstructures or molecular orbitals. All the outputs are displayed graphically in the simulator, providing a fast and intuitive understanding of the nano system.



When the user clicks the buttons on the user interface (for e.g. specifying the nanotube chirality), the program automatically generates atomic coordinates which can be visualized on the screen. When the user specifies particular electronic properties to be calculated, the program uses the automatically generated coordinates and runs tight binding in the background. The tight binding program is also quite universal. The user can choose schemes from many different parametrization schemes, including Harrison, Modified Harrison, Menon, Vogl, Tomanek, etc. Users can also control the number of K-points, basis functions etc. The final output is displayed on the screen, allowing the user to zoom in or out to see particular features.

The MSL Nanomaterials Simulator is made available to the research community through the NSF funded project -- Network for Computational Nanotechnology. Please contact kjcho@stanford.edu for this simulator. Main contributors to this program are [Bin Shan and Paul Leu at Multi-scale Simulation Laboratory]

For more information, please visit

<http://msl.stanford.edu>



Nanoparticle Simulator

File Nano Structure Simulation Help

Nanoparticle structure Generation

Element = Radius (A) =

Default Surface Energies (eV/A²)

100 110 111

Structure Information

Number of Atoms =

(100) surface Area (A²) =

(110) surface Area (A²) =

(111) surface Area (A²) =

Molecular Levels Calculation

Choose Your Paramatrization Scheme

Parametrization

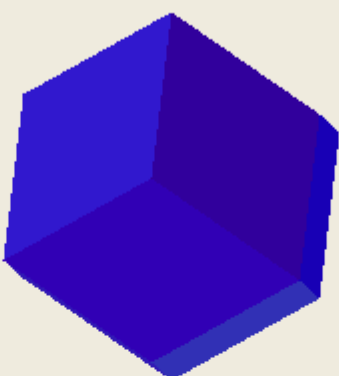
Electronic Structure

LUMO (eV)

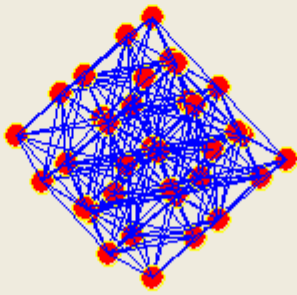
HOMO (eV)

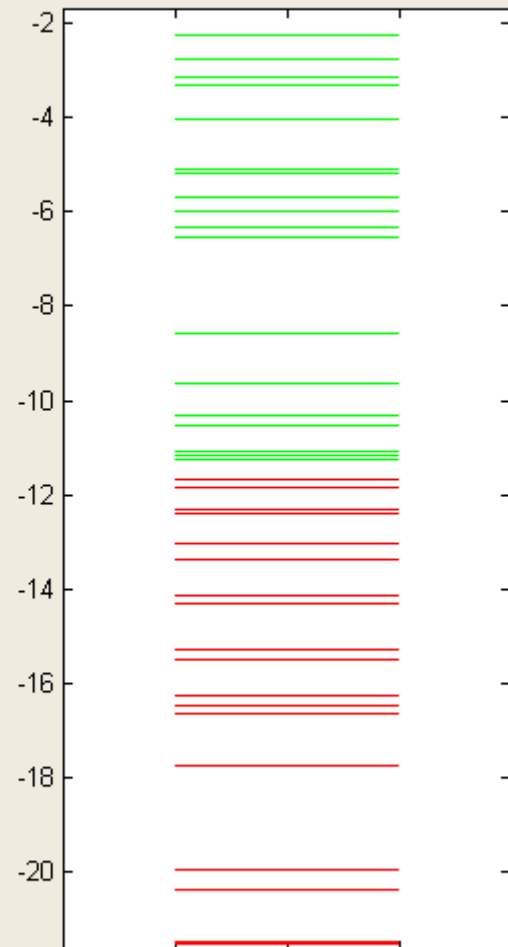
Energy Gap (eV)

Running Status :



dia





Harrison

Emin (eV)

Emax (eV)

Unoccupied Levels
Occupied Levels