Theory and Modeling of Weakly Bound/Physisorbed Materials for Hydrogen Storage

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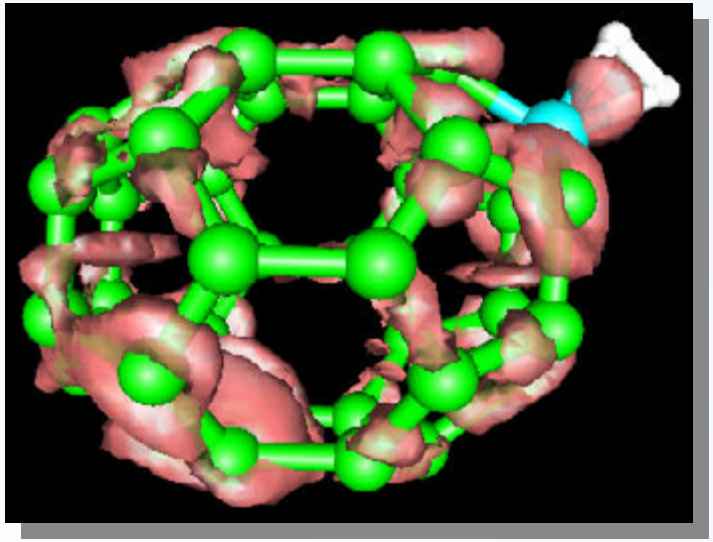

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Outline

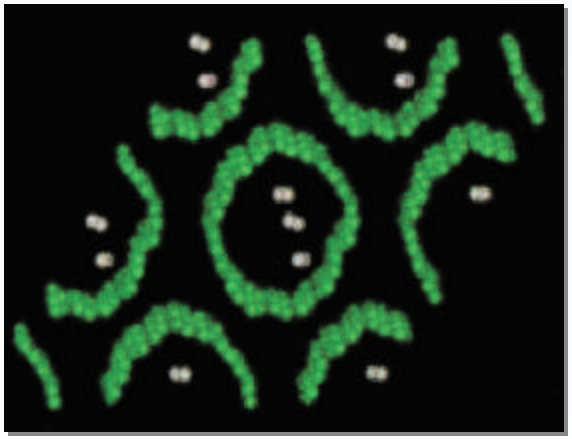
- Storage by physisorption:
  - CNT, fullerenes, carbon aerogels
  - Doping, Decorating, Charging
- Accuracy of Methods: DFT, QMC and Quantum Chemistry
  - Van der Waals interactions
  - LDA, GGA and ad-hoc corrections to pseudopotentials
- Use of DFT to screen for new compounds
  - Examples: H_2 binding to doped fullerenes
Opto-electronic properties of nanomaterials
- Zero point energies – the role of Path Integral QMC

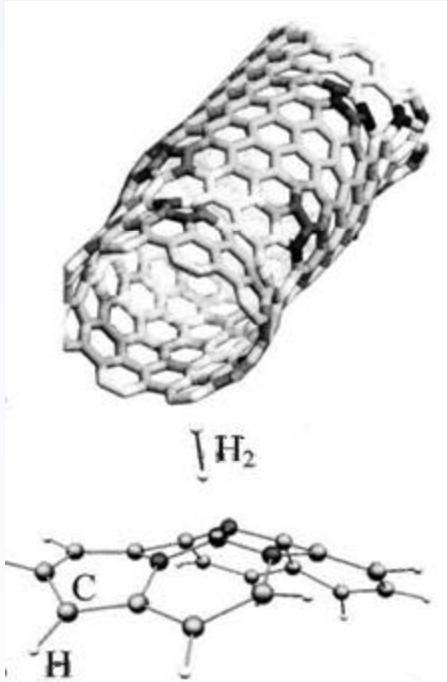
Energetic Requirements for Hydrogen storage

- Need to operate at near room temperature
  - Physisorption: Too weak C-H_2 : ~ 2 kcal mol^{-1} (70 meV)
  - Chemisorption: Too strong C-H : ~ 100 kcal mol^{-1} (4 eV)
- Need to find intermediate binding energies of 5 50 kcal mol^{-1} (0.1 0.5 eV)
- Carbon based materials offer several possibilities for manipulating binding energetics between H_2 and the material
  - Curvature
  - Damage
  - Doping
  - Decorating
  - Charging
- We want to use electronic structure calculations:
  - Predict the relative strength of each of these effects
  - Gain a fundamental understanding of interactions between H and materials

H_2 Storage by Physisorption: Pure Carbon

- Original CNT data[1] suggested 5 kcal mol^{-1} (0.2 eV) adsorption
- DFT (LDA)[2] calculations predicted instantaneous distortion and charge transfer can produce this unique binding
- Damaged CNT may have increased absorption[3]
- Carbon aerogels[4] have exhibited 5 wt% for high surface areas, ~1 wt% per 500 m^2/g

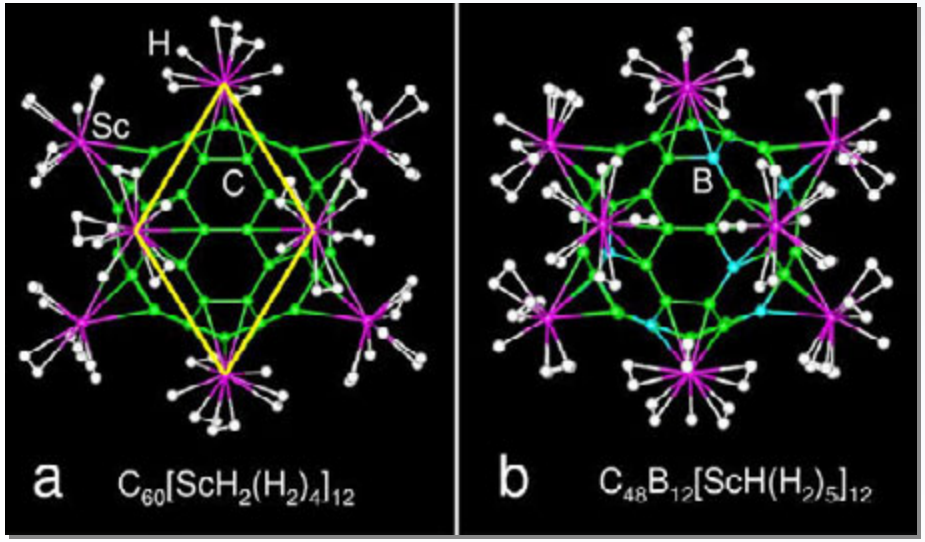


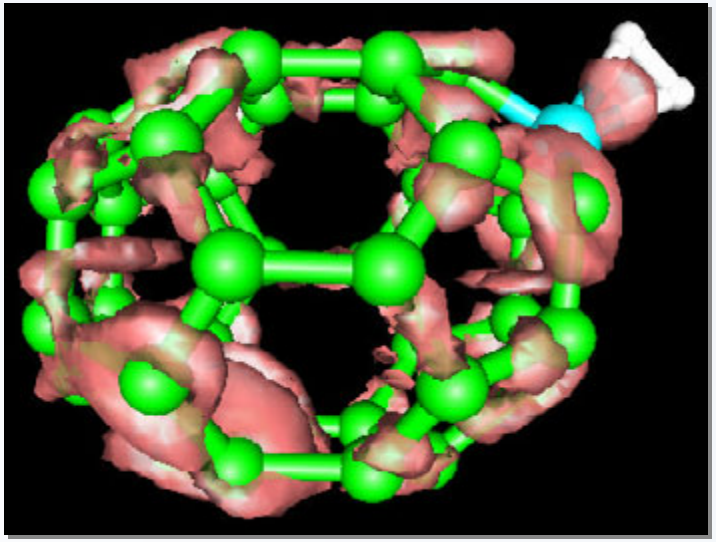


] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 377 (1997).
] H. Cheng, G.P. Pez, A.C. Cooper, JACS 123 5845 (2001).
] B.K. Pradham et al. Journal of Materials Research 17 2209 (2002).
] T. Baumann et al. (LLNL)

H_2 Storage by Physisorption: Carbon+

- DFT calculations of organometallic buckyballs[1], decorated with Scandium binding H_2 by 5 kcal mol^{-1} (0.3 eV) producing 9 wt%
- Doping fullerenes[2] can tune the binding energy of H_2 from 0 5 kcal mol^{-1} (0 0.3 eV)





] Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben, and S.B. Zhang, Physical Review Letters 94, 155504 (2005).
] Y.-H. Kim, Y. Zhao, A. Williamson, M.J. Heben, S.B. Zhang, 96 016102 (2006).

Computational Modeling of Hydrogen Storage

Modeling of physisorption is particularly challenging:

- DFT typically predicts accurate *structures*, but
- Van der Waals not included in mean field DFT approaches
- LDA and GGA calculations qualitatively disagree on *binding energies*[1,2]
- Need "beyond DFT" approaches
  - Quantum Monte Carlo (QMC)
  - Quantum Chemistry Techniques: Coupled cluster, CI

[1] B.K. Pradham *et al.* J. Mater. Res. 17, 2209 (2002)
[2] Y.-H. Kim, Y. Zhao, A.J. Williamson, M.J. Heben, and S.B. Zhang, Phys. Rev. Lett. 96, 016102 (2006)

Computational Methods

DFT Calculations

- Ab-init Code[1]
- LDA and GGA (PBE) exchange-correlation functionals
- Plane Wave basis set, 70 Ry cutoff
- Norm Conserving, TM pseudopotentials
- Relax atomic coordinates

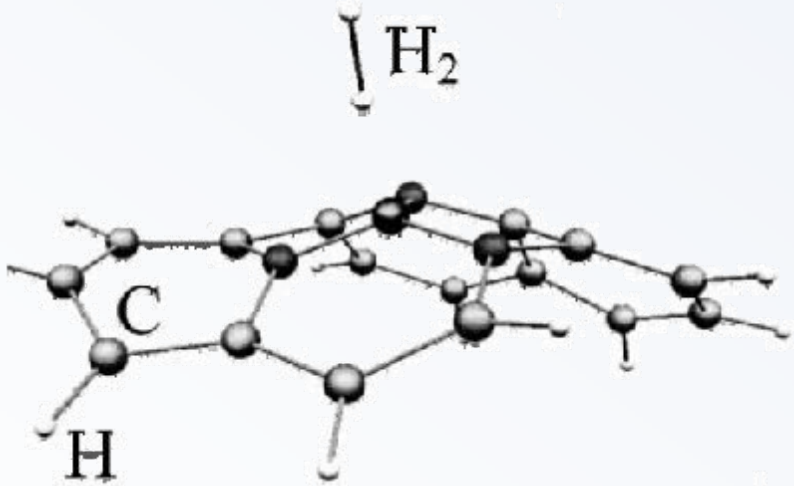
QMC Calculations

- Fixed Node, Diffusion Quantum Monte Carlo
- “Exact” many-body total energies
- Linear Scaling CASINO QMC code[2,3]
- Structures and single particle orbitals from DFT calculation
- Same norm conserving pseudopotentials

[1] Universite Catholique de Louvain, Corning Incorporated, http://www.abinit.org
[2] R.J. Needs, et al. *CASINO* version 1.6 User Manual, University of Cambridge
[3] A.J. Williamson, R.Q. Hood, and J.C. Grossman, Phys. Rev. Lett. 87, 246406 (2001)

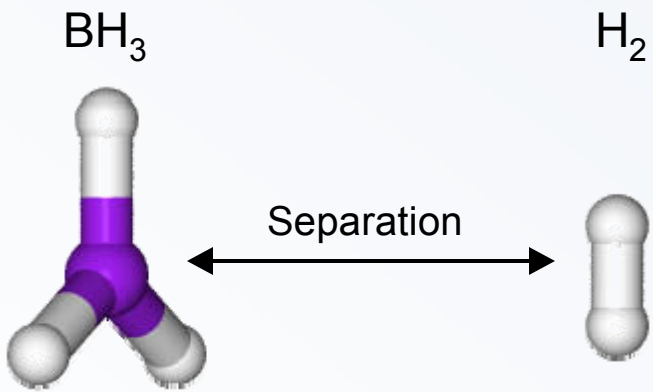
Test Case 1: Curved Graphene Sheet

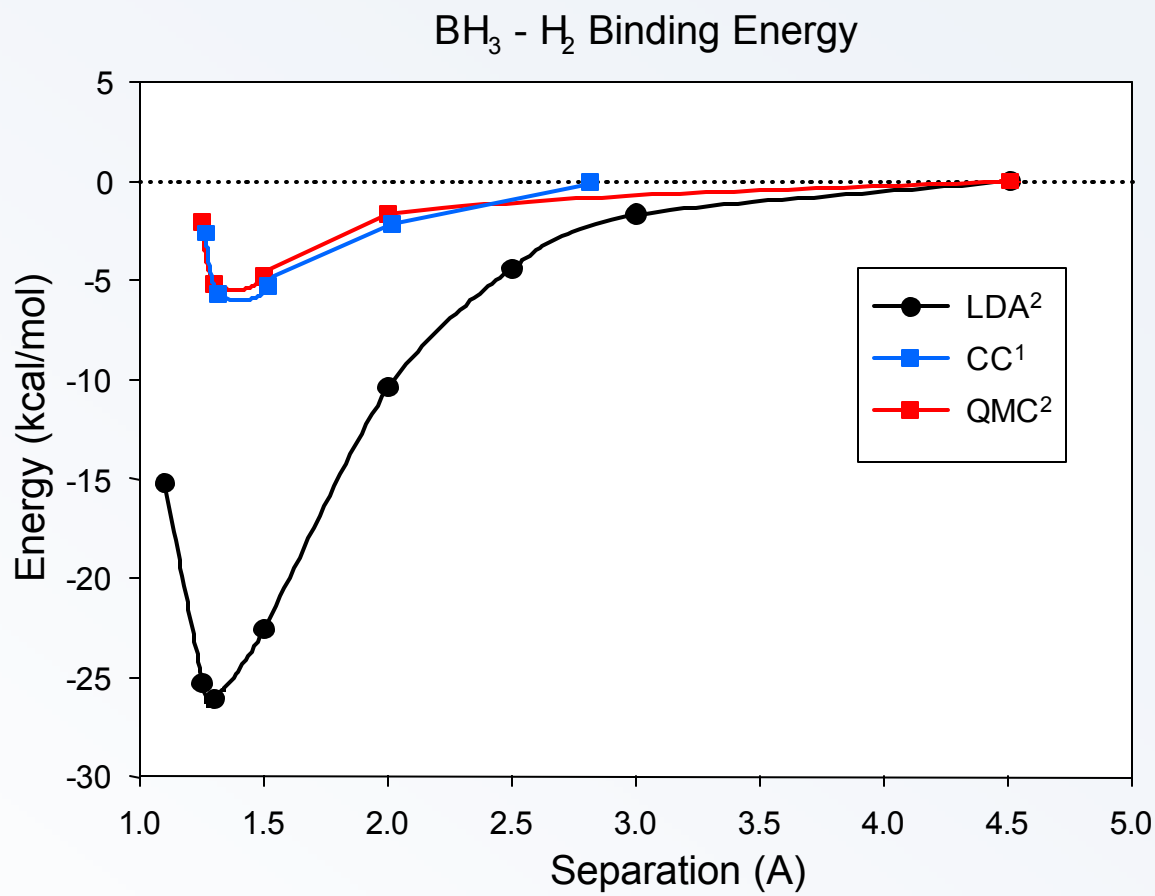
- Relax Structure in LDA (GGA structure not bound)
- Calculate binding energy in LDA, GGA, and QMC[1]
- Binding Energies:
  - LDA: 2.0 kcal mol^{-1} 0.09 eV
  - PBE: ~0
  - DMC: 1.6 kcal mol^{-1} 0.07 eV



[1] B.K. Pradham *et al.* J. Mater. Res. 17, 2209 (2002)

Test Case 2: BH_3-H_2



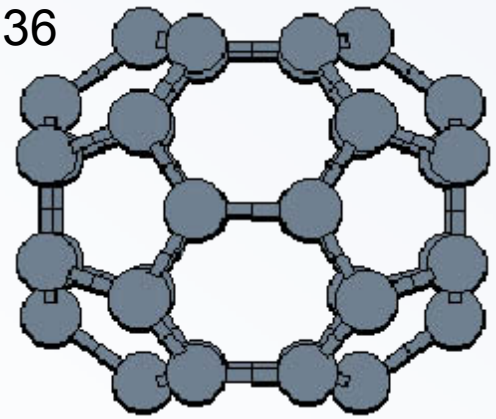


- Relax Structure in LDA
- Binding Energies:
  - LDA: 25 kcal mol^{-1} (1.1) eV
  - PBE: ~0
  - DMC: 6 kcal mol^{-1} (0.26) eV
  - CC: 6 kcal mol^{-1} (0.26) eV

[1] Kim et al, J. Phys. Chem. A 107, 301 (2003).
[2] Y.-H. Kim, Y. Zhao, A.J. Williamson, M.J. Heben, and S.B. Zhang, Phys. Rev. Lett. 96, 016102 (2006)

Using DFT to screen compounds: Doped C_{36} Fullerene

C_{36}



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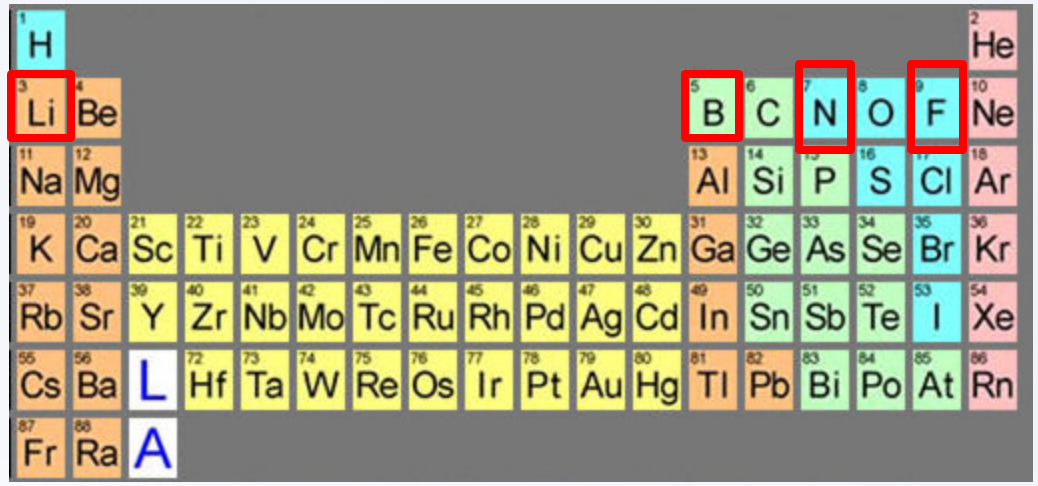
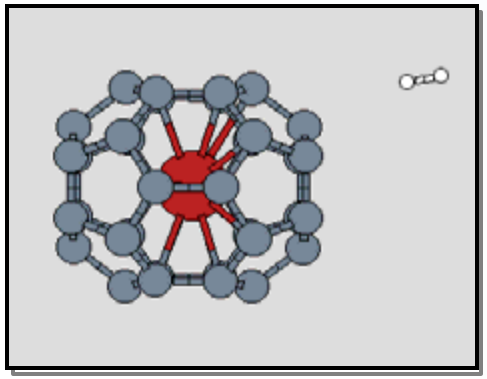
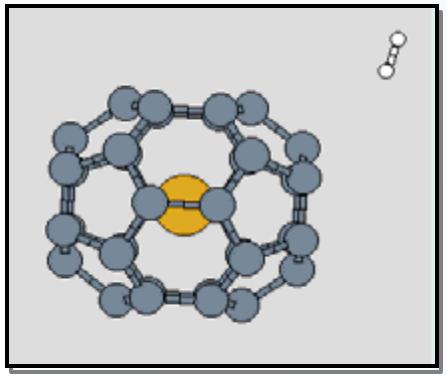


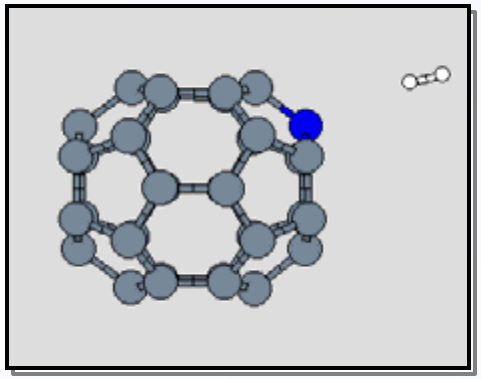
Endo-Li



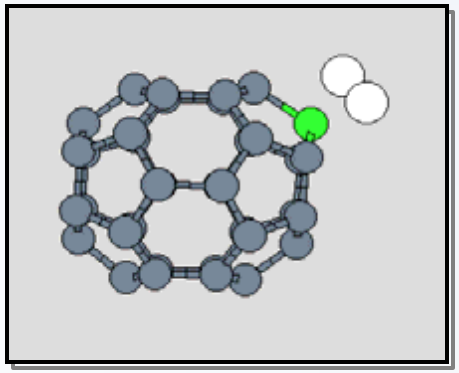
Endo-F



Sub-N

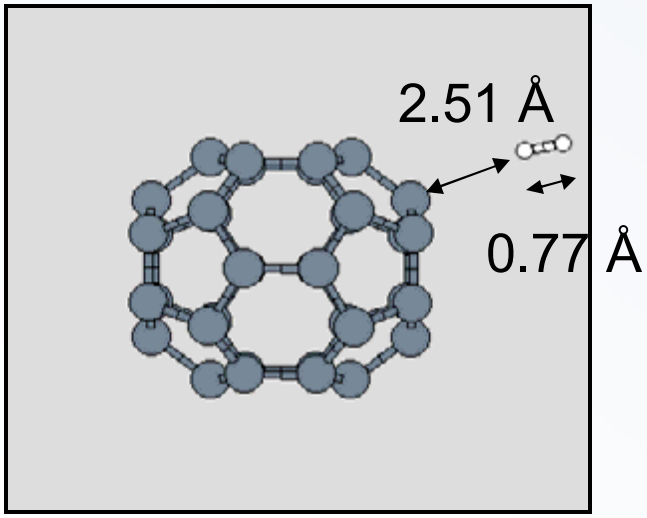


Sub-B



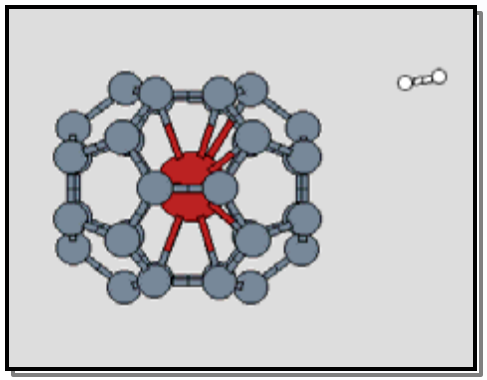
Weak interaction of H_2 with C_{36}

LDA: 65 meV



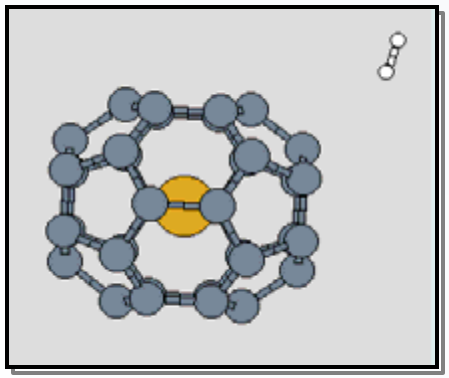
LDA predicts weak binding energy due to charge density overlap in DFT calculations.

Endo-Li



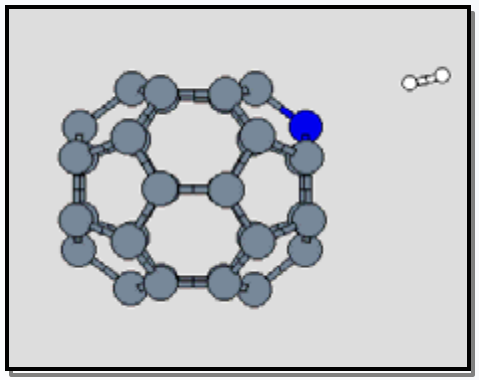
68 meV

Endo-F



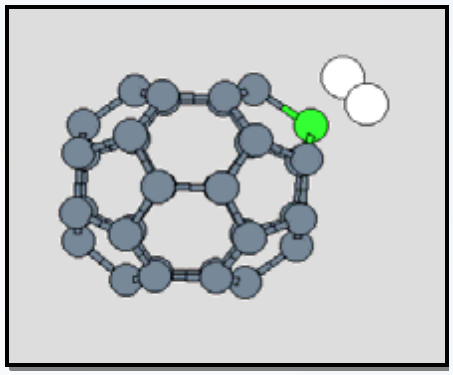
43 meV

Sub-N



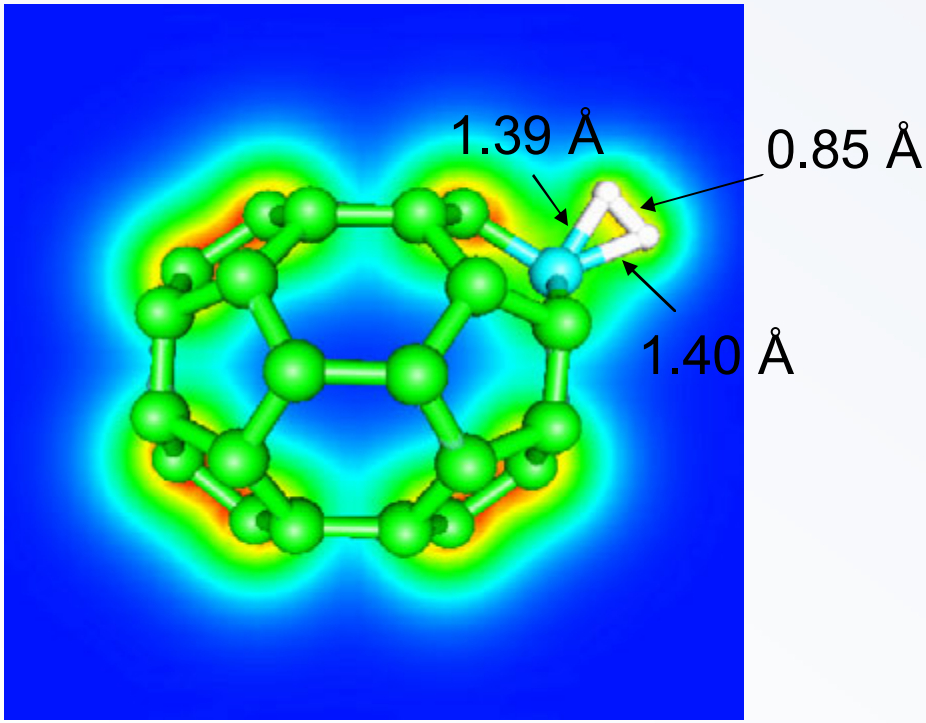
56 meV

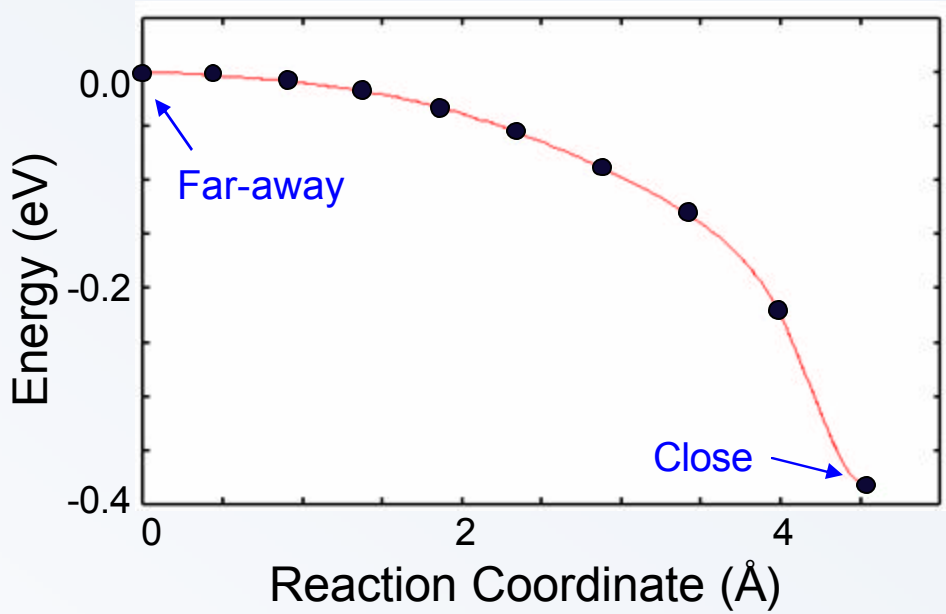
Sub-B



390 meV

Energetics of H_2 Binding to B-doped C_{36}



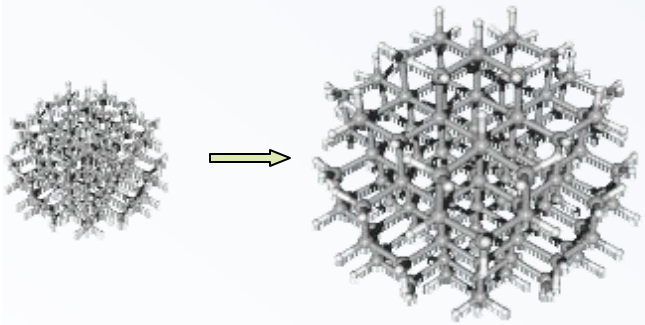


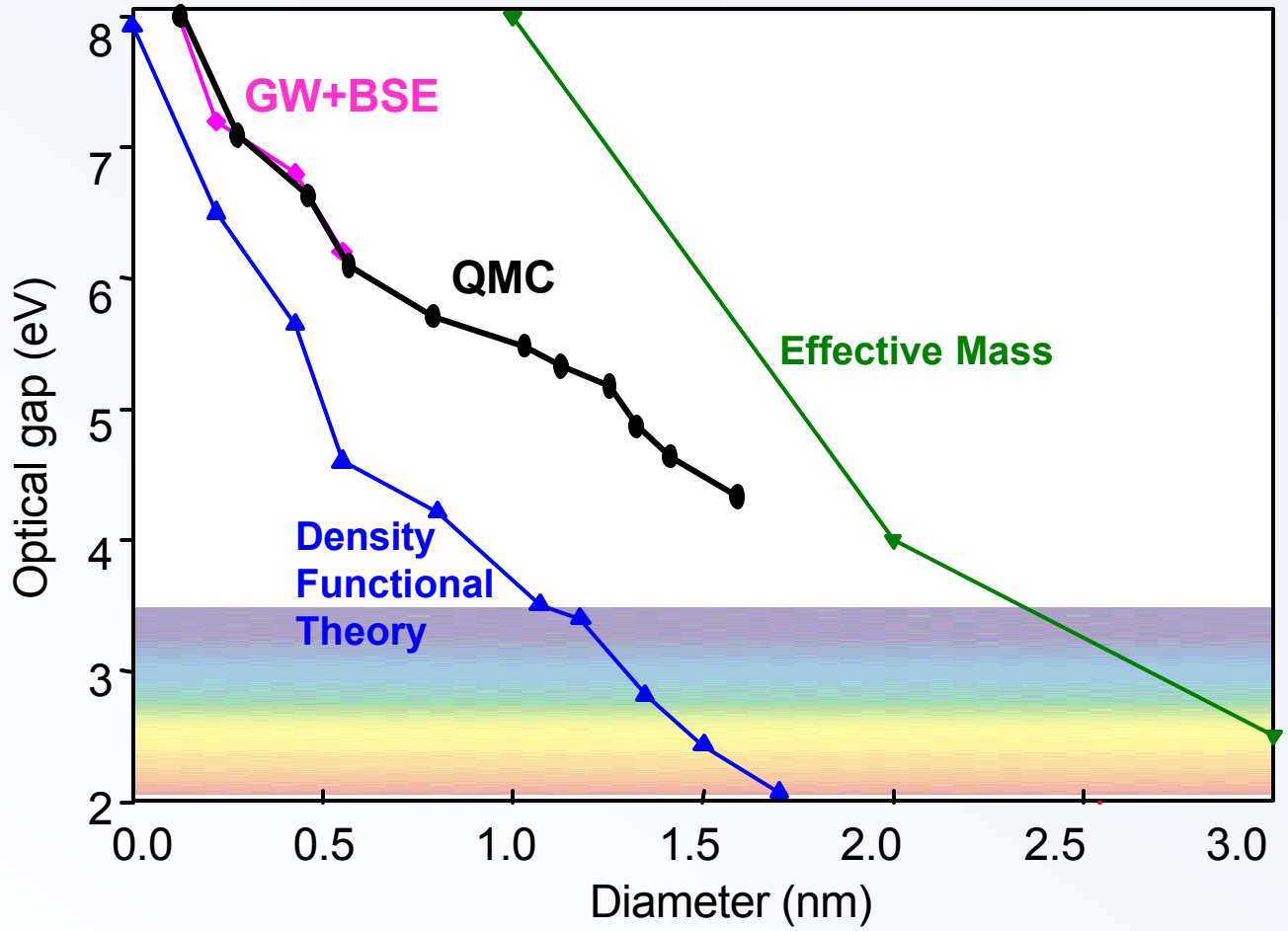
LDA Binding Energy[1]: 0.39 eV
PBE Binding Energy[1]: -0.03 eV
DMC Binding Energy[1]: 0.20(5) eV

- QMC and LDA agree on bond lengths
- No energy barrier to adsorption
- B-H length shorter than C-H
- H-H bond length increases
- DFT correctly predicts enhanced binding

[1] Y.-H. Kim, Y. Zhao, A.J. Williamson, M.J. Heben, and S.B. Zhang, Phys. Rev. Lett. 96, 016102 (2006)

DFT Trends: Size dependence of nanoparticle optical gaps



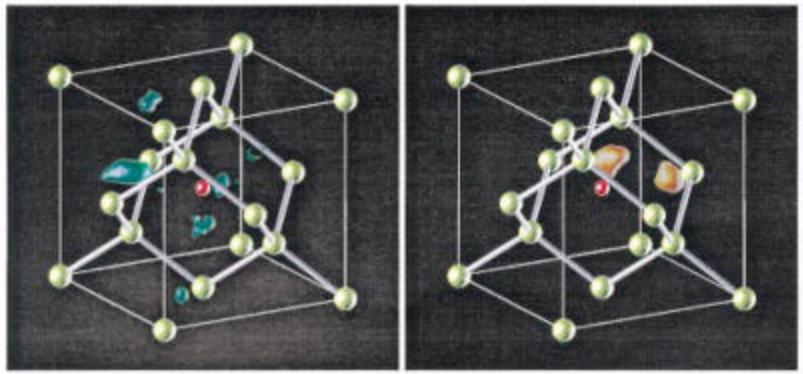


DFT underestimates gaps, but correctly predicts the size dependence

[1] A.J. Williamson *et al.* Physical Review Letter, 89, 196803 (2002)

Quantum Motion of Hydrogen Nuclei

- ZPE is ~0.2 eV – significant fraction of binding energy
- Ortho-para splitting is ~180K => strong changes in equilibrium concentration
- Potential energy surface for para hydrogen (groundstate) is shallower than ortho hydrogen
- Path Integral Techniques provide a viable solution for evaluating quantum effects
- Recent advances in DFT-PI-MD[2] or coupled electron-ion Monte Carlo offer possibility of including these effects in benchmark simulations



] T. Miyake, T. Ogitsu, and S. Tsuneyuki, Physical Review Letters, 81 1873 (1998)
] D. Marx, M. Parrinello, Journal of Chemical Physics, 104 4077 (1996)

Conclusions

- First-Principles computational modeling of H-Storage is vital for guiding and supporting experimental developments
- In weakly bound, physisorption materials, mean field DFT calculations can accurately predict structural properties, vibrational frequencies, but not energetics
- DFT appears to predict the trends in energetics – typically somewhere between LDA and GGA values
- DMC calculations provide a mechanism for accurately calibrating the electronic contribution to binding energetics
- Path Integral calculations required to include the quantum motion of the hydrogen nuclei

More details: www.llnl.gov/qsg