Simulations of the Staebler-Wronski effect

attempts at an atomistic picture

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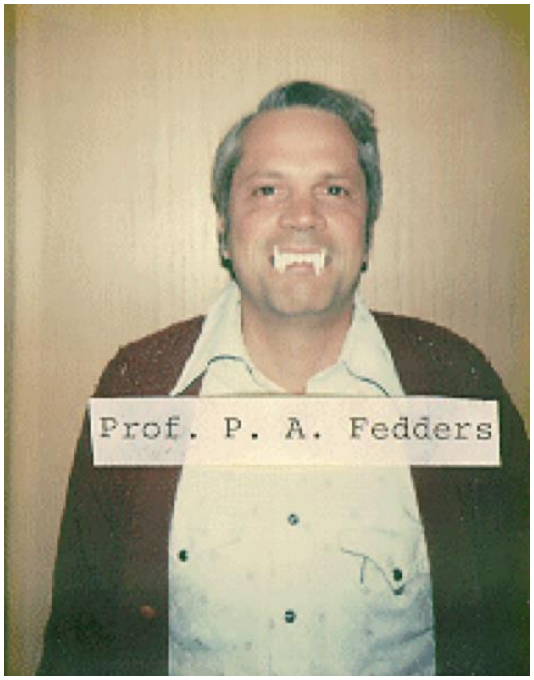
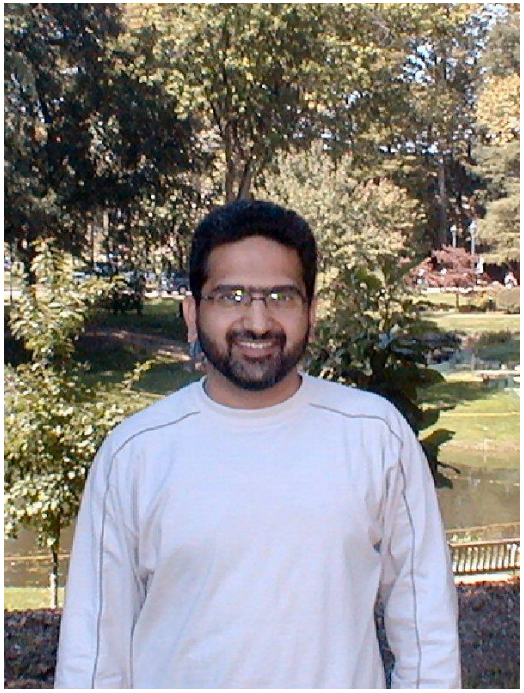
Collaborators



Distinctive personality who started these approaches, *ca.* 1992.



F. Inam – PhD student

Roadmap

- Background material on topology of a-Si:H, electron states, band tails and the electron-phonon coupling.
- Our approach
- Where we are, what to do.

A vast field

- We know a lot about a-Si:H from years of experiments and theory. Almost too much (10,434 hits on WOS as of March 13 at 11.49AM)!
- The work of synthesis is therefore especially important (eg, *thank you* H. Fritzsche, B. Street, M. Stutzmann, W. Fuhs…)

Some background from simulation

- Nuts and bolts of simulations
- Structure of a-Si:H
- Electrons in a-Si:H; filamentary states
- Electron-lattice interaction
- The static and dynamic role of H in the network

Simulation nuts and bolts

- Cells with 64-1000 atoms
- Periodic Boundary Conditions
- Code: SIESTA [DFT, local basis set, double-zeta polarized (13 orbitals per site), PBE GGA]
- Tests with VASP [DFT, plane wave basis set]

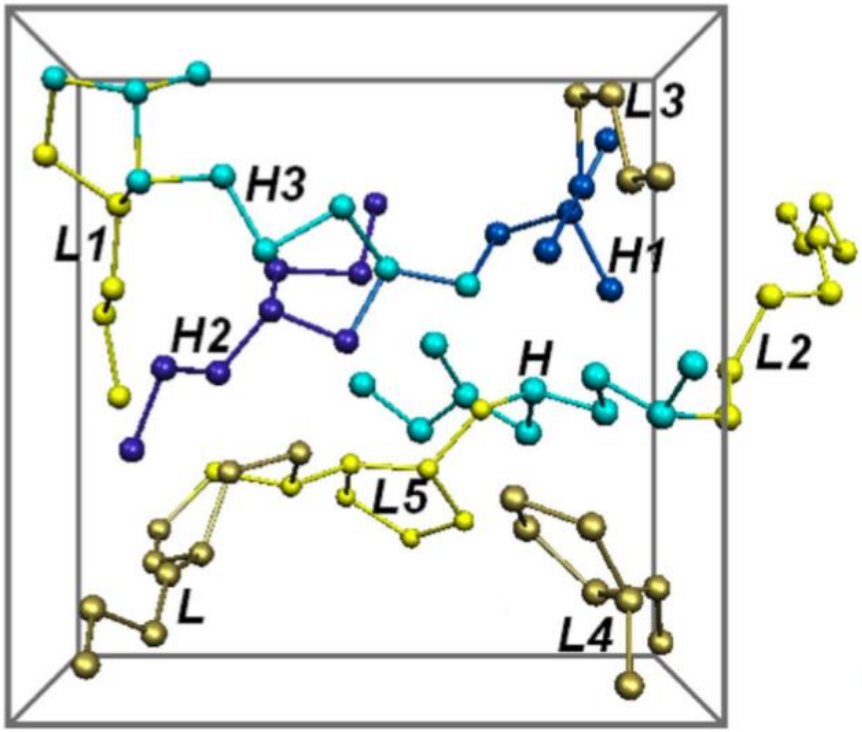
Hidden features in a-Si structure

String theory is for us too…

- Tail eigenstates in the most realistic models are on 1-D filaments of long and short bonds we name electron filaments (long bonds, conduction; short bonds, valence).
- There are structural filaments of long and short bonds present in the models.
- The Urbach (exponential) tails are associated with these filaments.

Two filament systems

- Electron filaments



PRL **100** 206403 (2008)

- Structural filaments

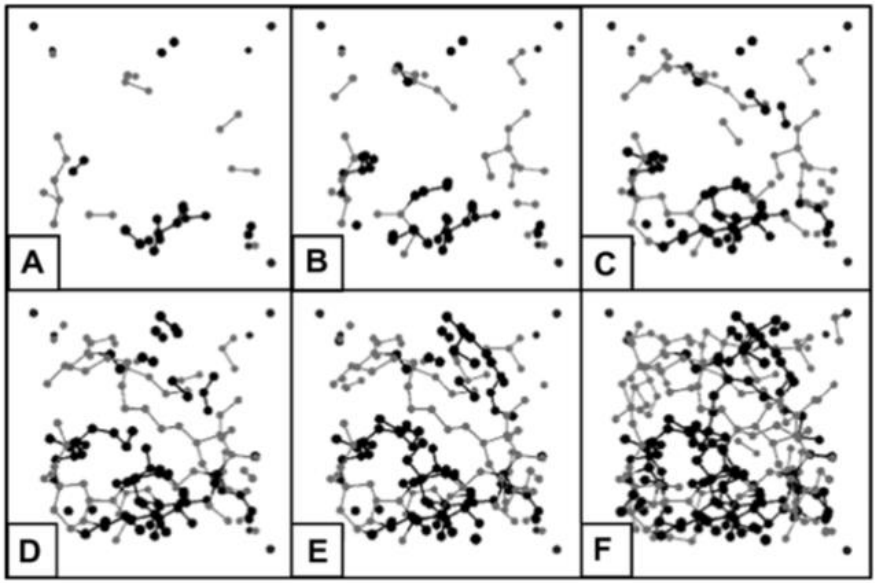
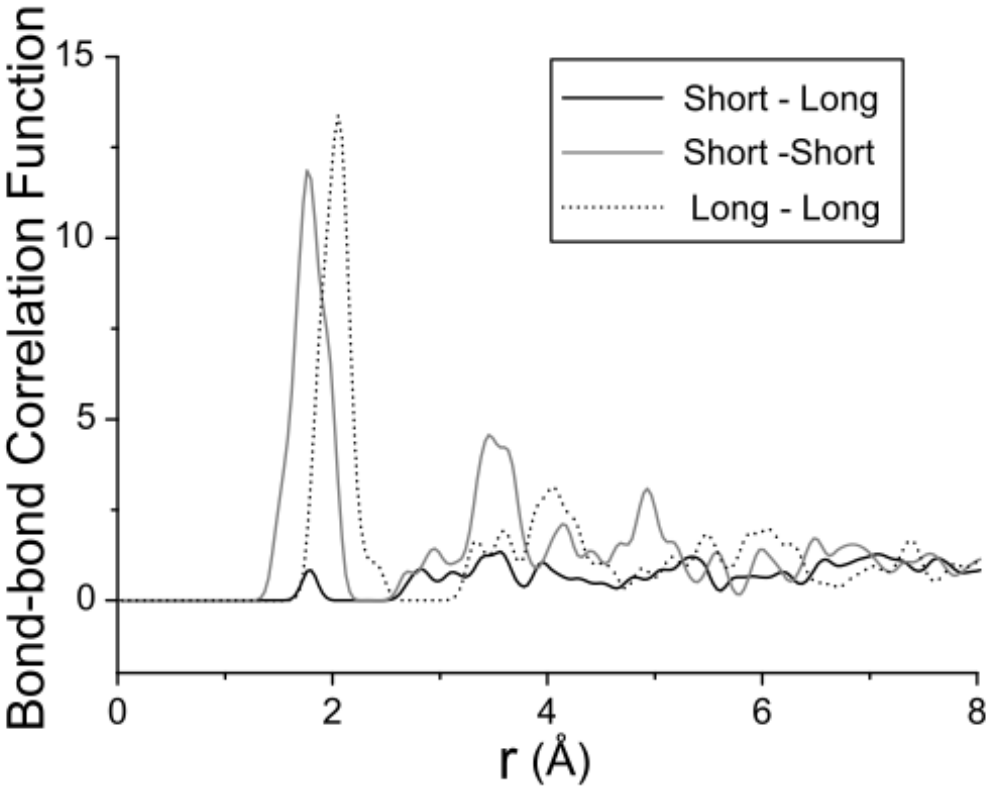


Fig. 2. (A) 1%, (B) 2%, (C) 3%, (D) 4%, (E) 5% and (F) 8% shortest(dark) and longest (light) bonds of model M_1.

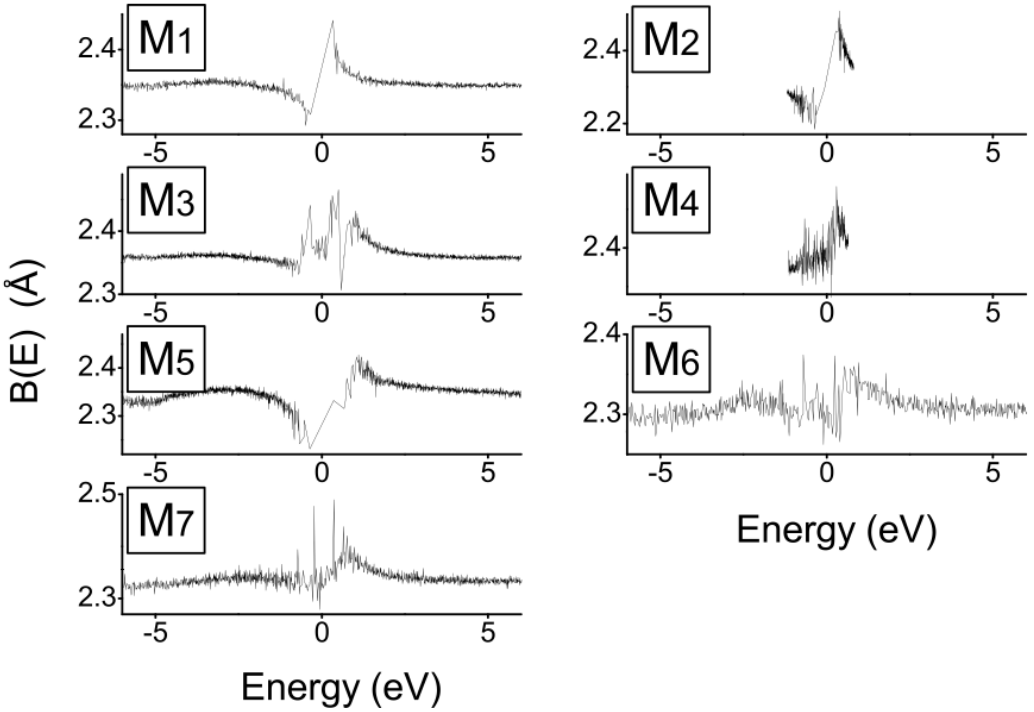
JNCS **354** 3480 (2008)

Correlation functions (l-l, s-s, s-l)



In 512-atom DTW model strong correlation of long bond to long, short to short.

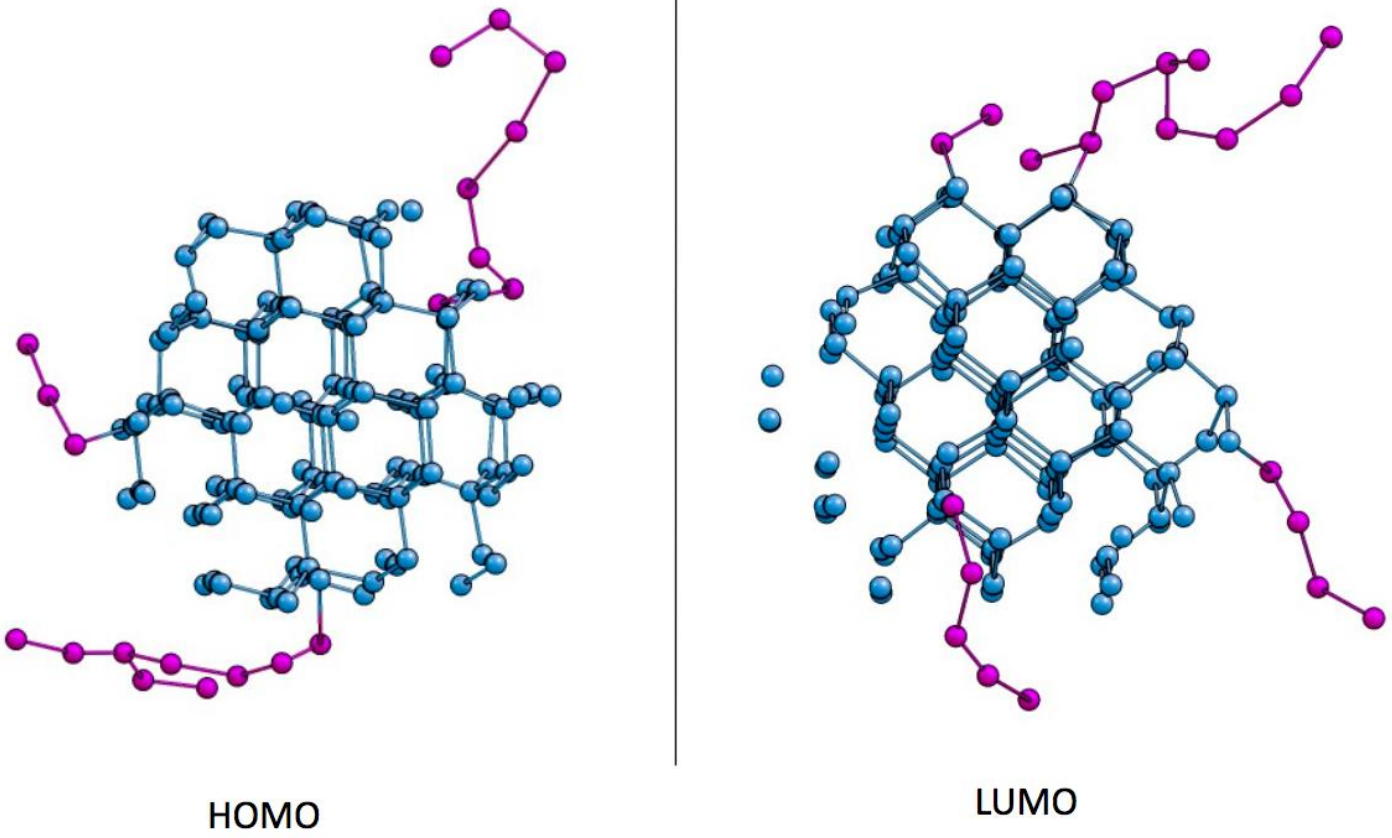
Bondlength decomposition of tail states as a function of energy



$$B_{(E)} = \frac{\sum_{n,m} b_{(n,m)} q_{(n,E)} q_{(m,E)}}{\sum_{n,m} q_{(n,E)} q_{(m,E)}}$$

Electron strings and crystallites: Si

the role of inhomogeneities



1000 atom cell: CRN+123-atom crystallite embedded; only atoms in xtal and atoms contributing to HOMO and LUMO states are shown. (*S. Chakraborty, unpublished*)

Structure of a-Si:H

- Wooten-Weaire-Winer CRN provides excellent model for a-Si (*sans* H); recently we have made a-Si:H without "bias": release unbonded atomic H into network, let it "go"

J. Phys.: Condens. Matter **21** (2009) 084207

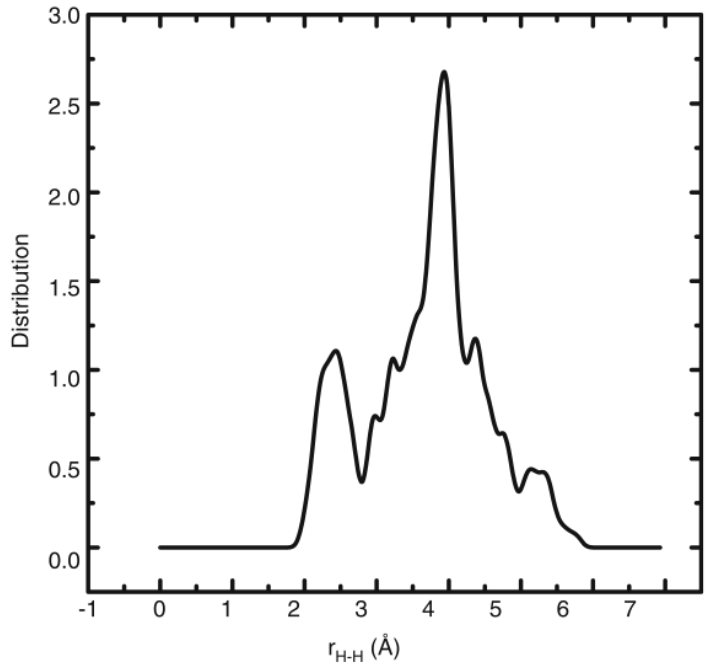


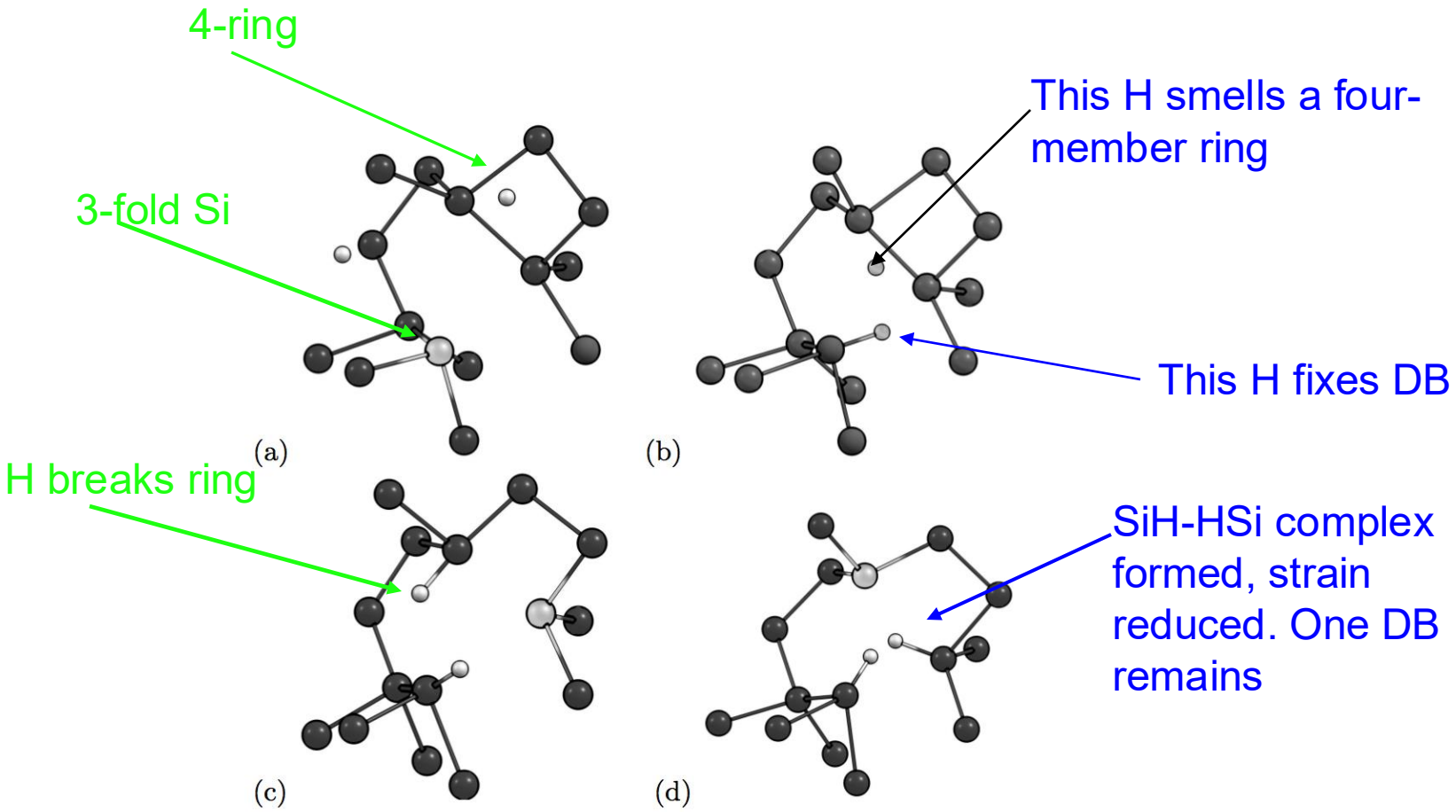
Figure 14. Distribution of minimum H–H distances in amorphous Si216H24 model averaged over 0.30 ps at $T = 300$ K.

After lots of bond forming/breaking: creation of stable distribution of clustered and diffuse protons (*broad and narrow NMR lines*)!

Voids: H the strain detector/killer

S. Chakraborty, DAD PRB **79** 115214 (2009)

Start with relaxed divacancy, release the H, kill the four-member ring:



Example of H dynamics with heterogeneous system: H_2 Formation in large void interior

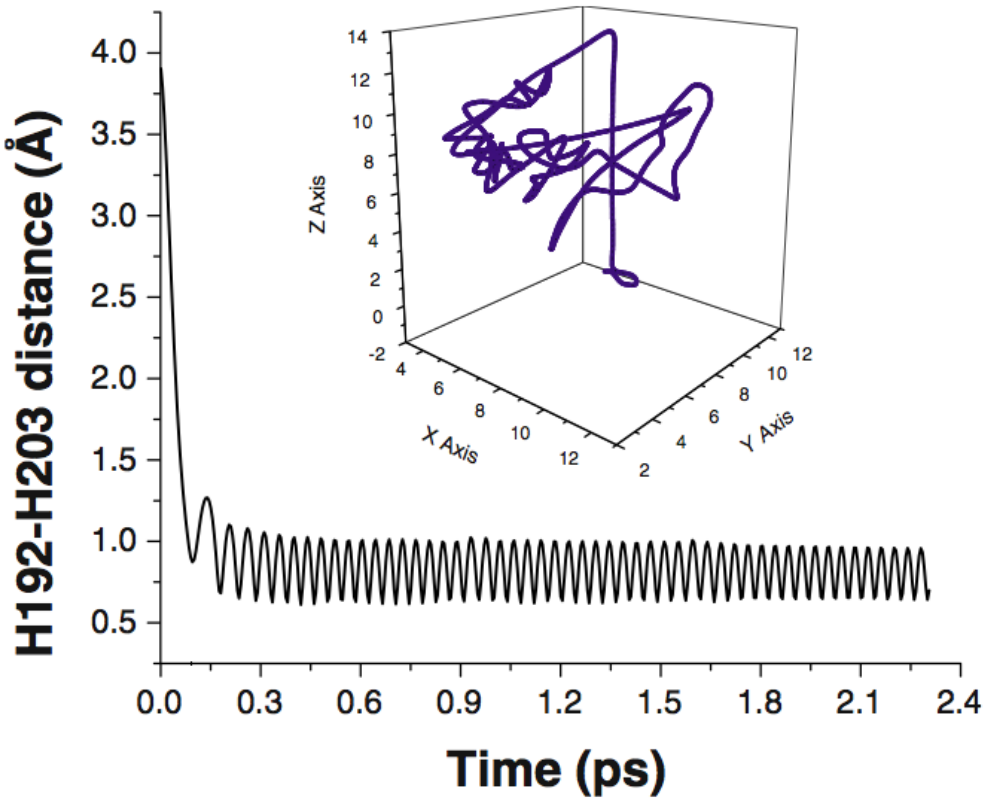
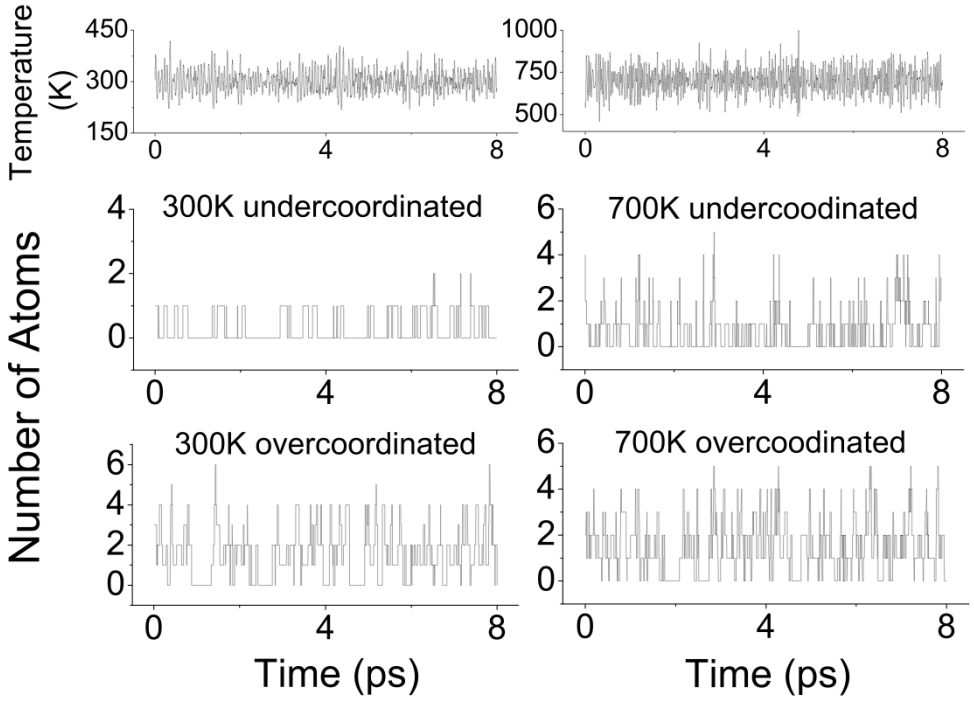


FIG. 8. (Color online) Plot of H-H distance between H_{192} and H_{203} showing the formation of the molecule. The trajectory of the two H in the H_2 molecule is shown in the inset. After H_2 formation, motion is confined to the void interior.

Coordination fluctuations



Constant (T,V) simulations: SIESTA. R_c=2.75Å

J. Non-Cryst. **354** 2149 (2008)

RMS fluctuations: Si ions

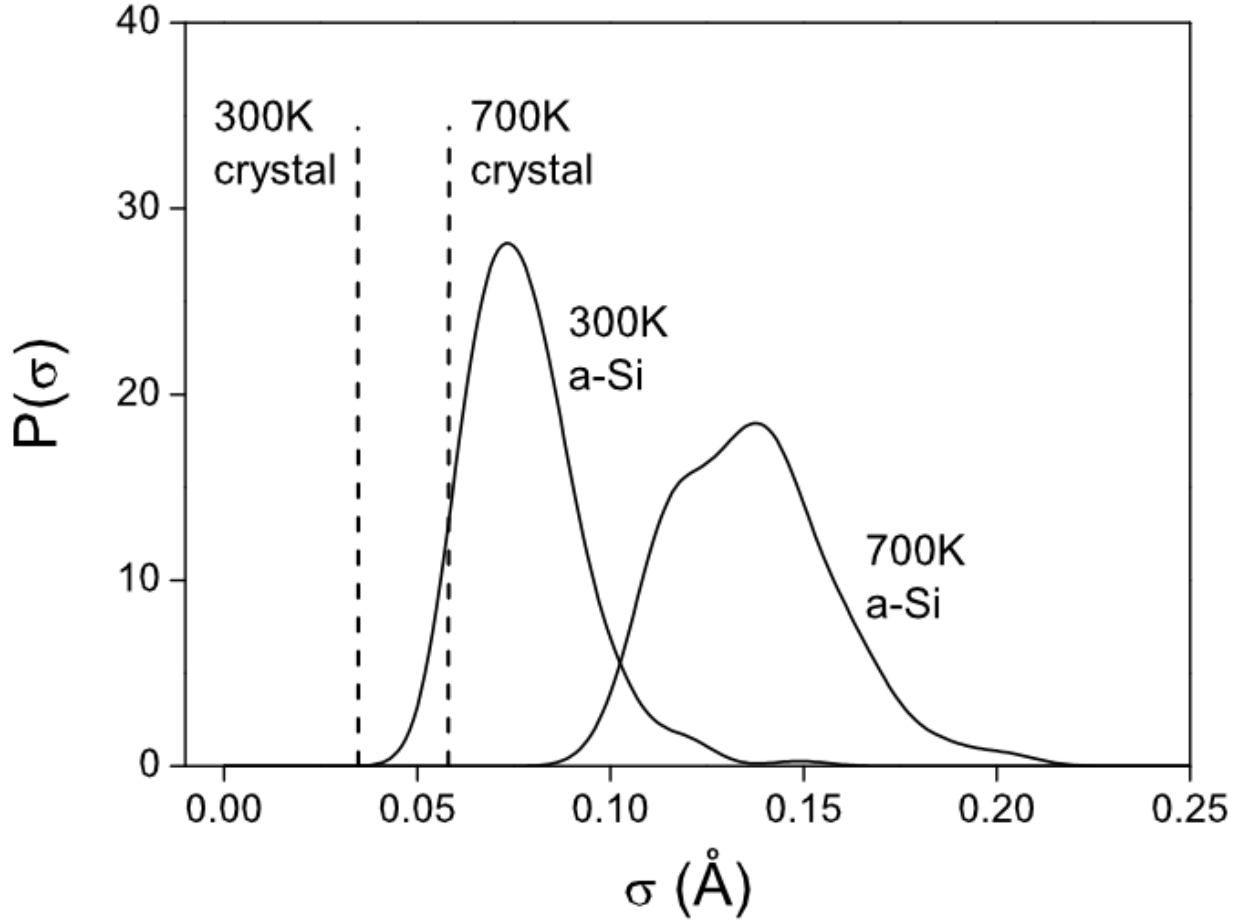
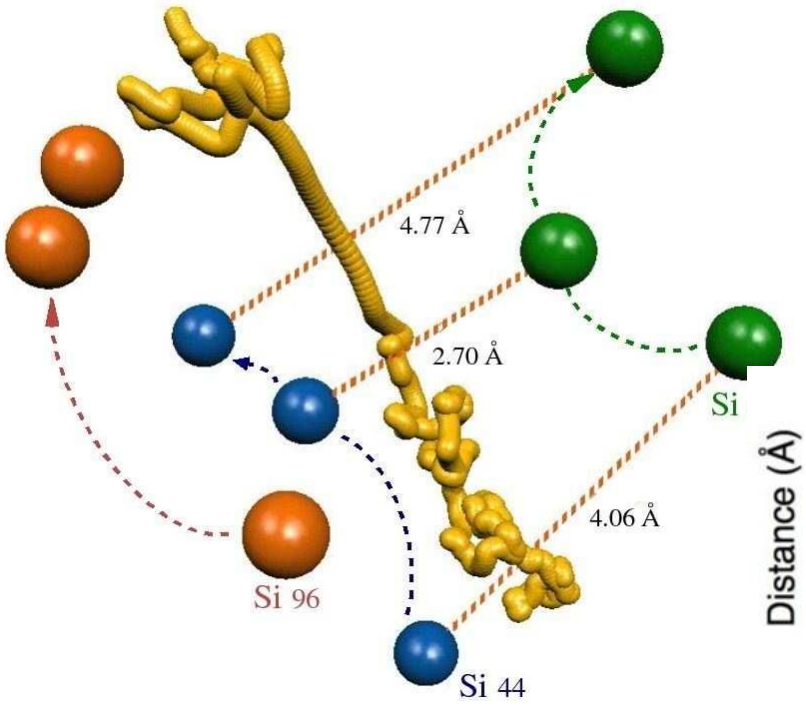


Fig. 3. Distribution of root-mean-square fluctuations σ in the ionic positions in 216-atom model at $T = 300$ K and $T = 700$ K, for both diamond and a-Si and constant T simulation, using empirical potential [25]. The data was acquired over 200 ps.

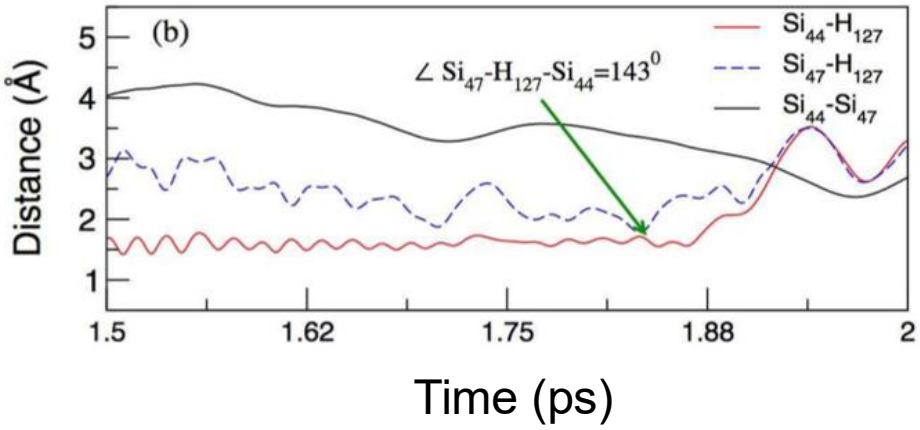
H dynamics: Fluctuating Bond Center Detachment "FBCD"

Converting bonded H to diffusing H



Explicit example. Yellow worm: path of H_{127}

1. H passivates DB on Si_{44}
2. H becomes BC when Si_{47} "transits"
3. BC H hops, bonds to Si_{96}



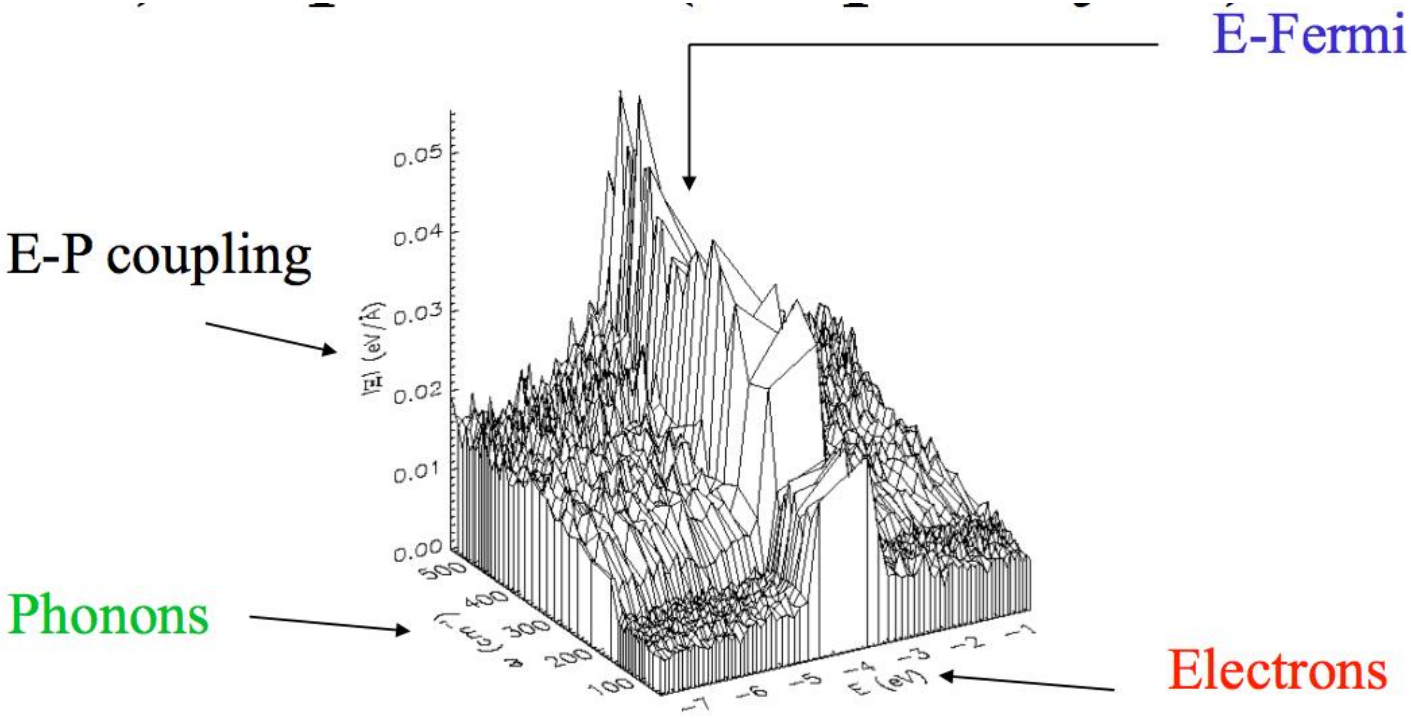
FBCD: Discussion

- Highly temperature-dependent (at 300K, one event, 1000K, nine events in 6.25 ps)
- Reminiscent of a mechanism of Su and Pantiledes based upon "floating bonds". FBCD is more general.
- Connected to SWE (??) -- if network is heated in any way, will stimulate H motion.

Electron-phonon coupling and SWE

- Light affects the electronic structure of the material
- The modified electronic structure leads to changes in network structure and dynamics. Somehow, in fact, to new defects.
- Thus E-P coupling $\Xi_n(\omega)$ (electron *n*, phonon ω) is a piece of the puzzle needed to model SWE.

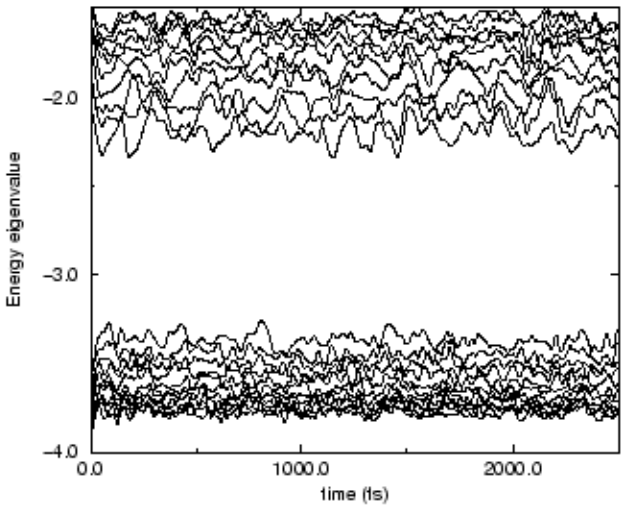
Electron-phonon coupling is large for localized states



$$\Xi_n(\omega) = \sum_\alpha \langle \psi_n | \partial H / \partial R_\alpha | \psi_n \rangle \, \chi_\alpha(\omega)$$

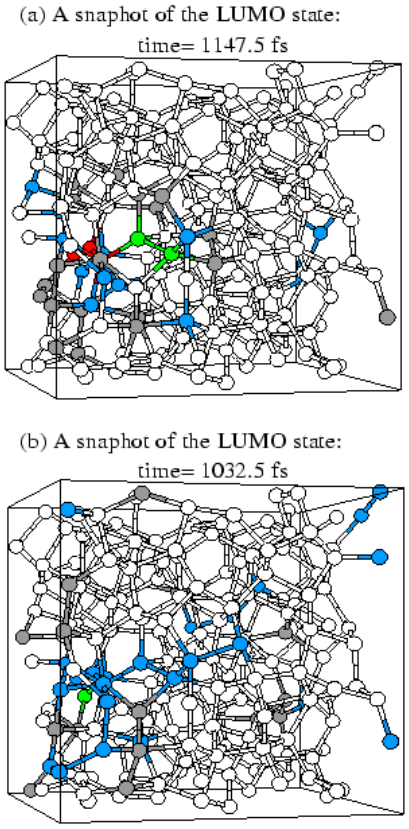
Couple electron n (energy E) and phonon ω

E-P coupling: thermally induced fluctuations in the spectrum

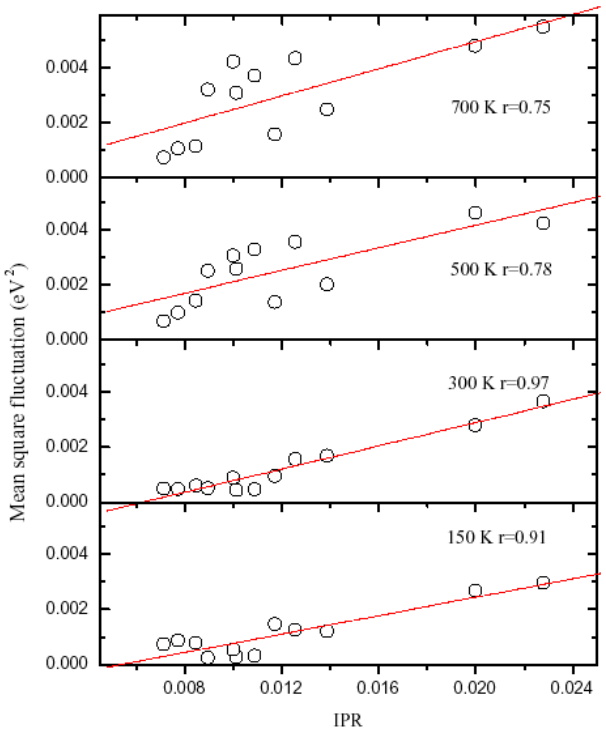


Thermally-induced fluctuations in Kohn-Sham eigenvalues (300K). 216-atom cell.

$\sigma >> kT$!



Fluctuations in CBE eigenvector



Correlation between IPR (localization) and RMS fluctuations.

So what?

- Only localized electron states have large coupling to lattice. *No SWE in crystal or in a material with so many defects that impurity bands form.*
- Thermally-induced variance of eigenvalue *n* is

proportional to the localization "IPR": $< \delta\lambda_n^2 > \propto IPR_n$

Also for squared E-P coupling: $\Xi_n^2 \propto IPR_n$

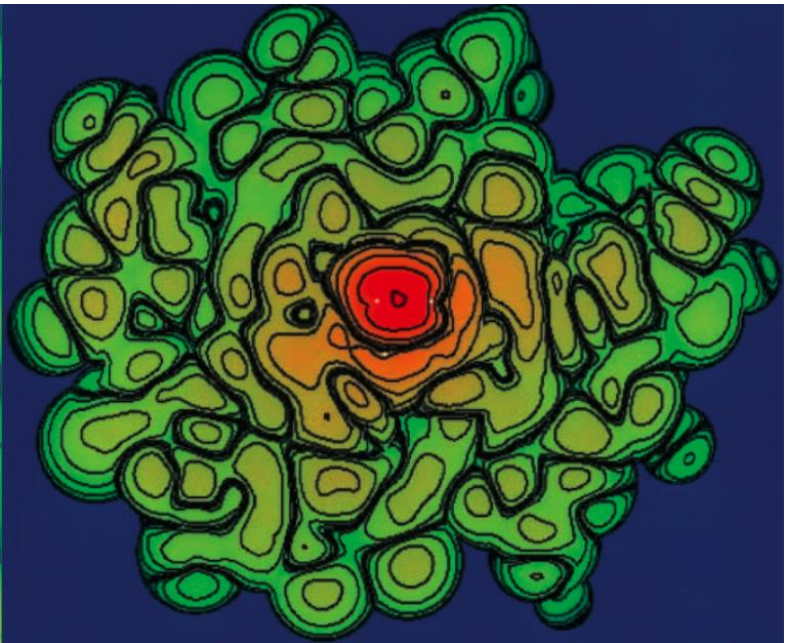
- Links a T=0 property (localization of a state) to T>0 property fluctuations in eigenvalues.

Locality of interactions in a-Si

Kohn's *Principle of Nearsightedness* for a-Si

- Calculations of the density matrix[1] or generalized Wannier functions[2] provide quantitative information about locality of interactions in a-Si: $\rho(\mathbf{x},\mathbf{x}') = 2\sum_{n-occ}\psi_n^*(\mathbf{x})\psi_n(\mathbf{x}') = 2\sum_n w_n^*(\mathbf{x})w_n(\mathbf{x}')$

- Asymptotic decay is exponential: $\rho(\mathbf{x},\mathbf{x}') \sim \exp(-\gamma|\mathbf{x}-\mathbf{x}'|)$



Wannier function in 4096-atom WWW model of a-Si: decay is exponential, γ~0.45/Å. *Similar to crystal!*

Thus, ~10Å is the range of interactions in a-Si.

[1]X. Zhang, DAD Phys. Rev. B **63** 233109 (2001).
[2]U. Stephan, R. M. Martin, DAD Phys. Rev. B **62** 6885 (2000).

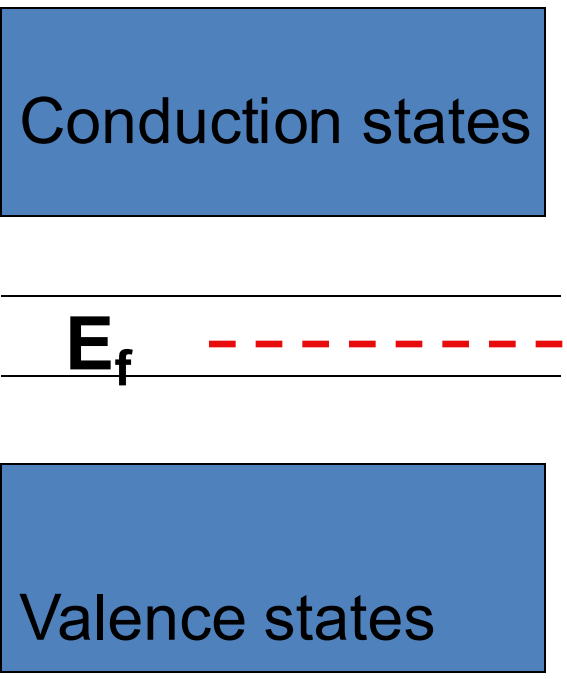
SWE: simulation technology

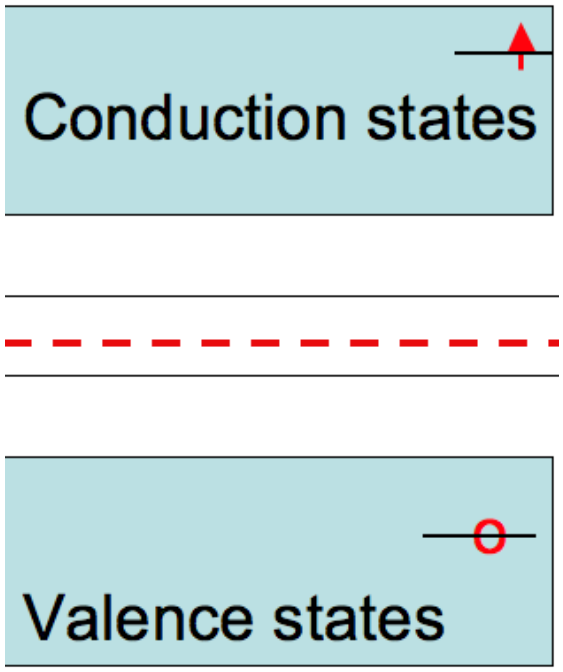
- Computer models genuinely consistent with a-Si:H (structure, phonons, electrons/optics)
- Reasonable approximations for wave functions, electron-phonon couplings, charge densities, spin densities.
- Density functional methods do quite a good job on Si-H systems -- in the ground state.
- Care is needed in approximations (Chris) -- use SIESTA and DZP basis, with PBE GGA.

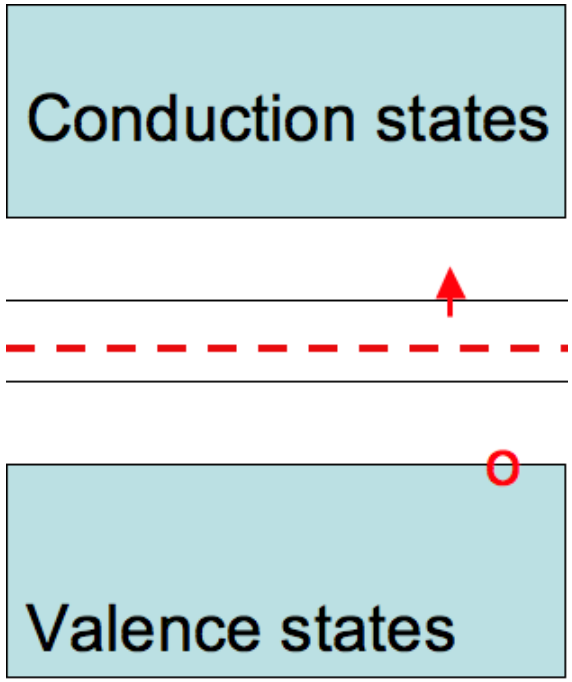
What we can -- and cannot -- do

- We *cannot* offer credible excited states in this framework.
- We *cannot* "properly" represent the light-solid interaction (*eg*, the quantum process of light-inducing electronic transitions).
- Non-adiabatic dynamics is possible but difficult for large systems like ours.
- Can't simulate nanosecond (or longer) dynamics directly.

A model for light-induced changes







t=0 electronic ground state

$t=t_0$: light creates e-h pair

$t=t_0+\Delta$; system thermalizes, leaving uncorrelated e and h.

Discussion

- Light creates e-h pair; this thermalizes in time Δ with hole near VB edge (state ψ_h), electron near CB edge (state ψ_e) .
- It is likely that ψ_h and ψ_e are localized.
- It is likely that $|\mathbf{x}_h - \mathbf{x}_e| > 10$Å; the electron and hole are uncorrelated: this is *not* an exciton (an e-h bound state).

Discussion (continued)

Thus, it is reasonable to model the post-thermalization dynamics by local volumes with holes and other volumes with electrons.

In a given ca. 10^3 atom cell, it is reasonable to model SWE by ground state calculations with extra or missing electrons, *not both in the same small cell*.

This model suggests that charge injection and light-induced changes are closely related.

In our model*: hard excited state problem = multiple uncoupled ground state problems with different charge states.*

Questions

- Are occupation changes in valence or conduction tail more likely to cause bond breaking/switching?
- How is H bonding and dynamics influenced by occupation changes?
- How are the results of our simulation the same (and different) from SWE, and charge injection experiments or even experience of doped systems?
- When do our approximations fail?

First attempt: no H

PAF, Fu, DAD PRL **68** 1888 (1992)

Using simplified DF Hamiltonian on strained 63-atom cell: Change in charge state of well-localized leads to quick succession of bond breaking, highly non-local (after ~300 fs, changes across cell)

TABLE I. Essential properties of one series of computer-simulated light-induced defects.

	Configuration				
	0	1	2	3	4
Number of geometrical defects	2	2	4	4	4
Time in fs	0	100	200	400	200
Number of spectral defects	3	3	6	5	6
Temperature (K)		200	200	200	300

Evidence of local heating

Abtew *et al.*, JNCS **354** 2149 (2008)

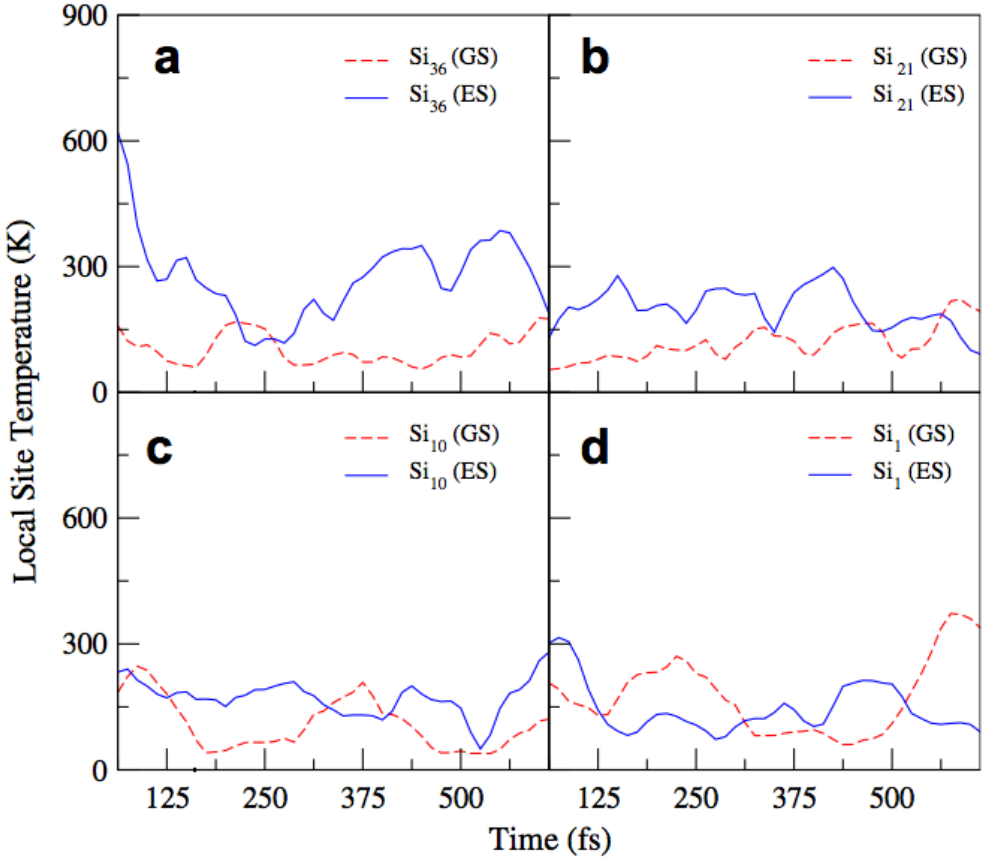
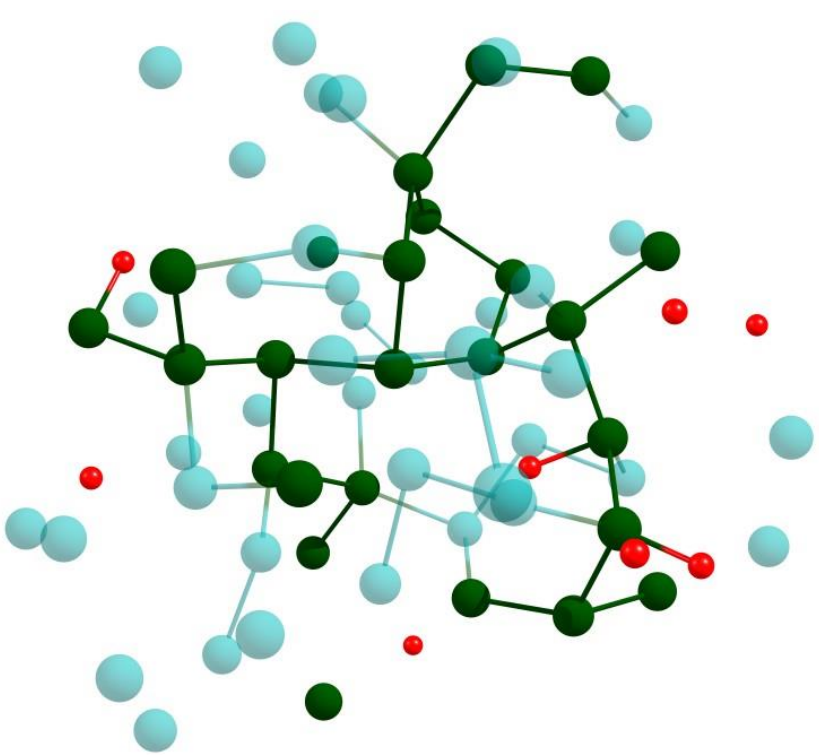


Fig. 5. Local temperature (kinetic energy) at dangling bond site (Si_{36}) and other sites unconnected with the localized state centered on Si_{36}. GS means electronic ground state, ES, excited state.

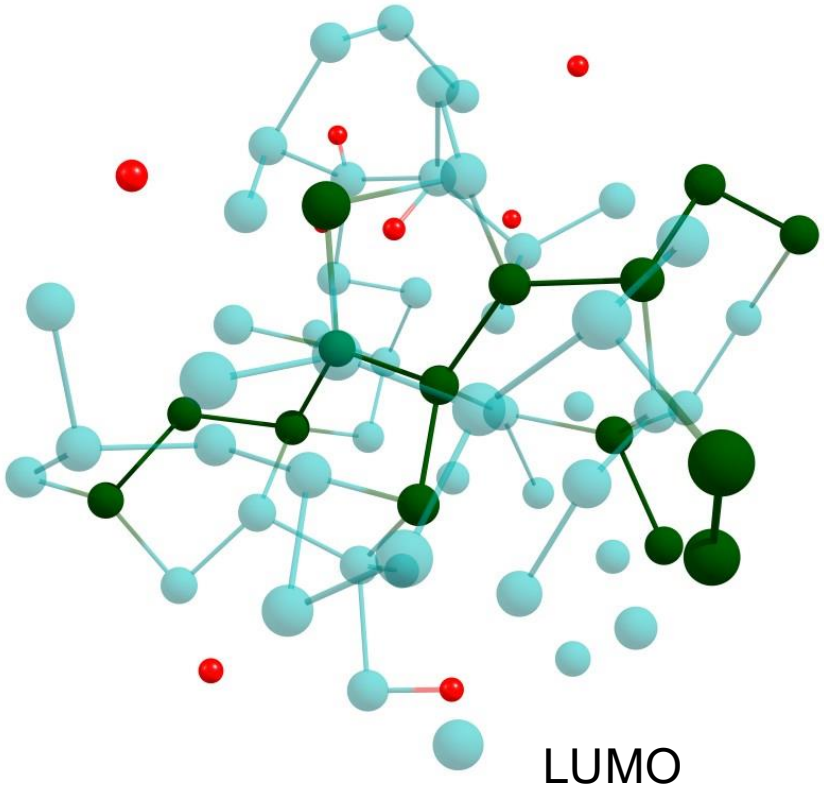
New models

- Earlier models: H introduced manually "God's Scissors" -- to repair defects [have recently learned of "Marshall's (Stoneham) hand"].
- If one simply releases free H into the network, we eventually get a reasonable distribution of clustered and dilute H -- both NMR lines. Have 64, 216 atom models.
- We use these models in the rest of the talk.

Frontier orbitals, small cell $Si_{64}H_8$

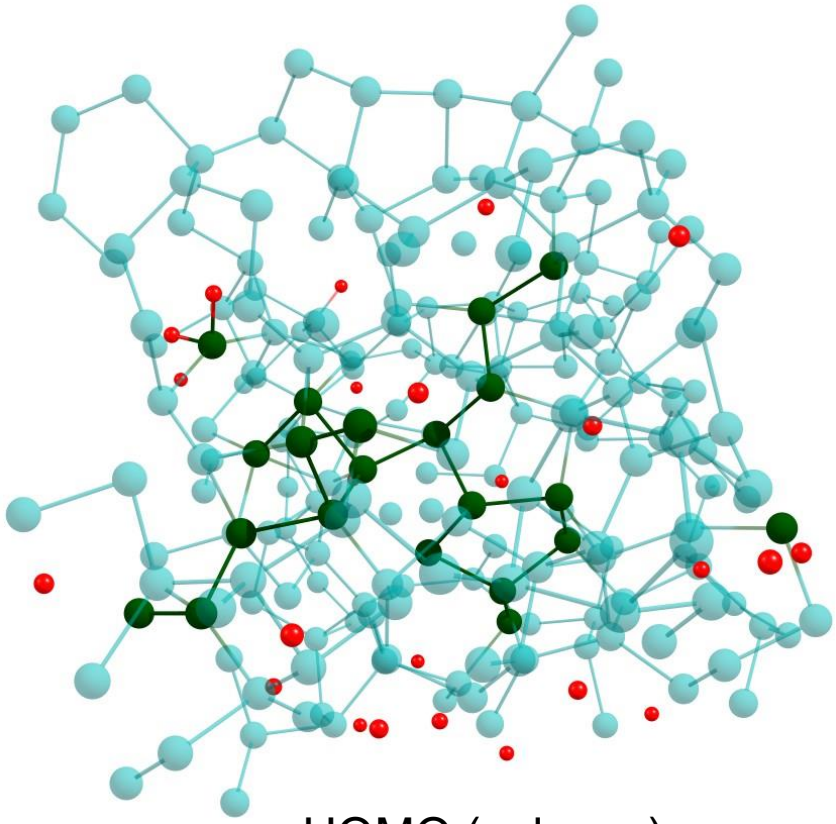


HOMO

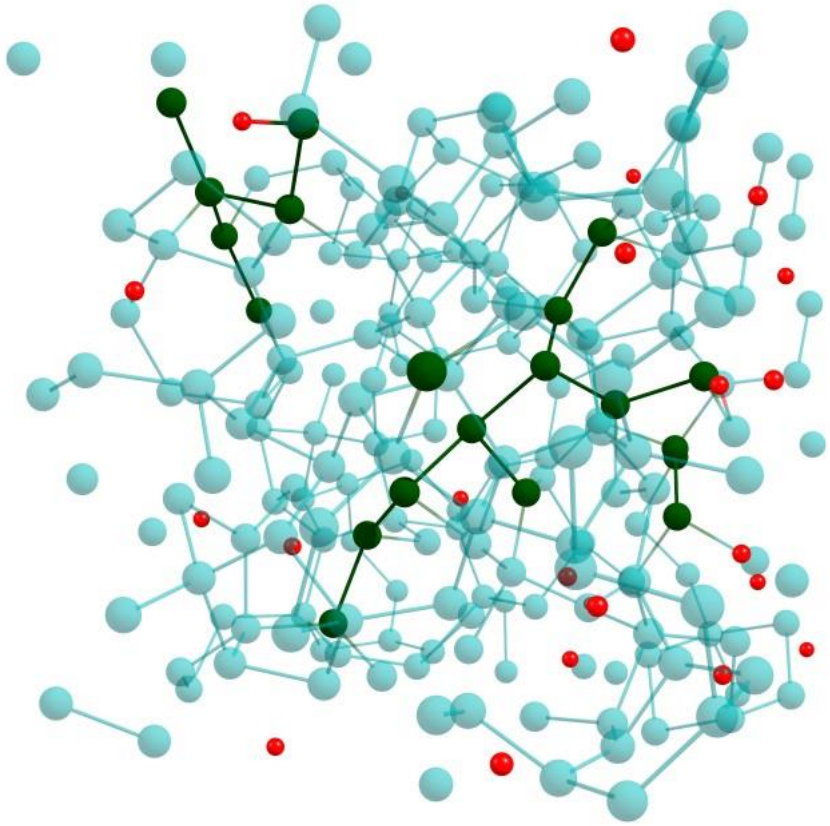


LUMO

Frontier orbitals, large cell $Si_{216}H_{24}$



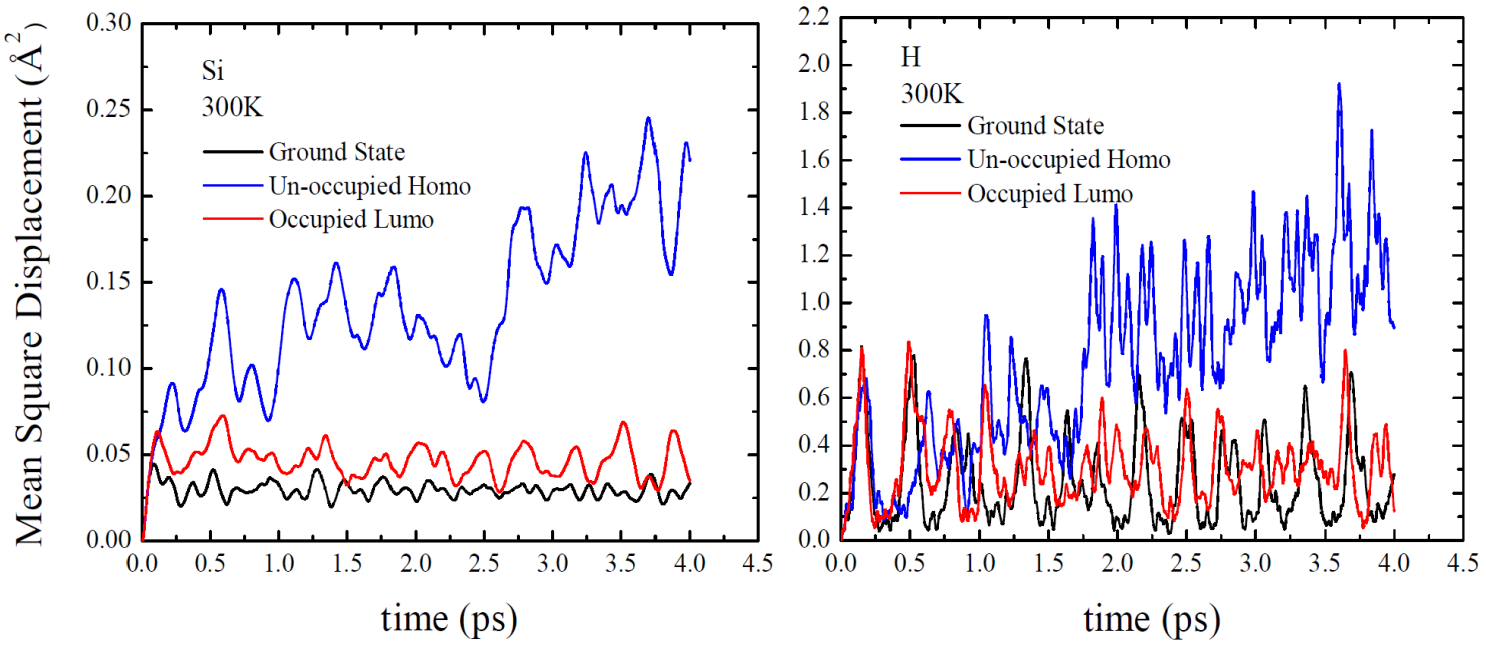
HOMO (valence)



LUMO (conduction)

Dynamics of varied charged states

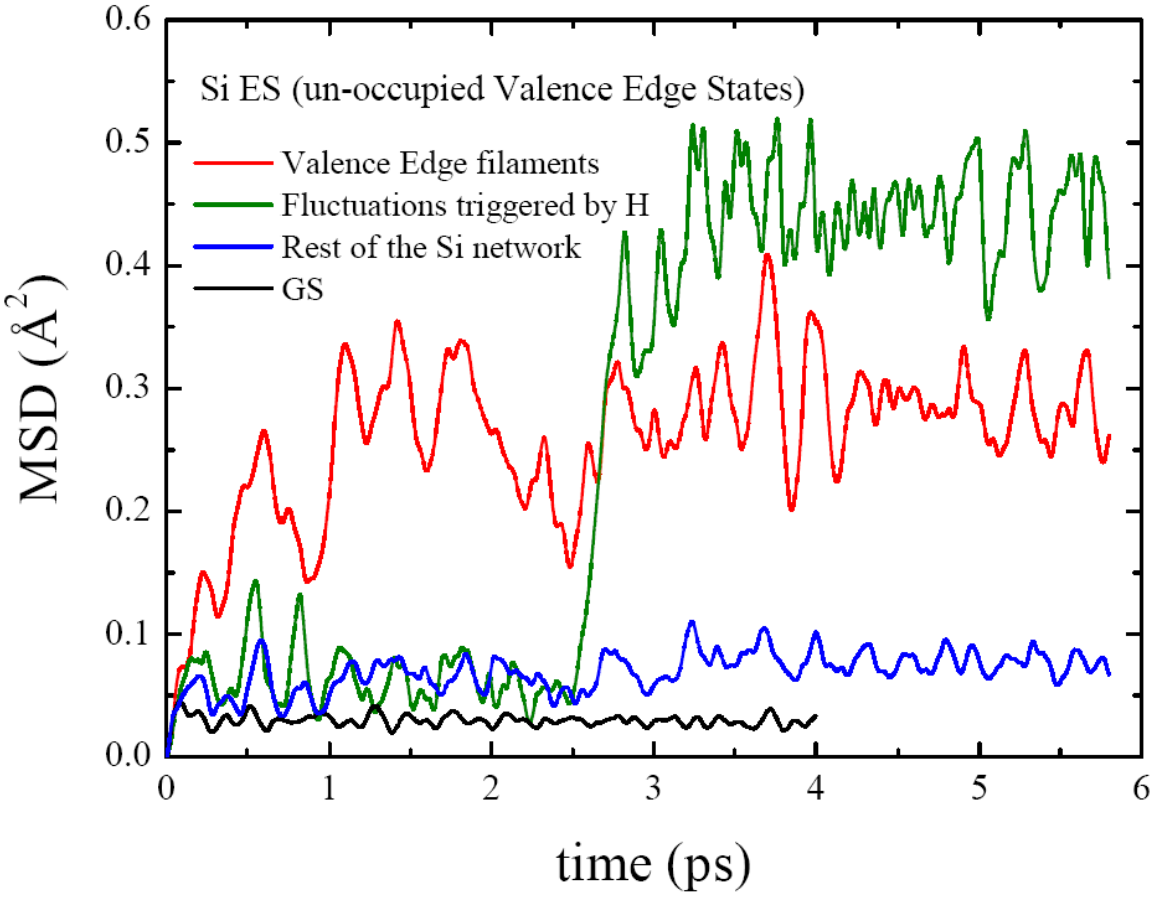
- Unoccupied valence edge states (holes) exhibit enhanced thermal fluctuation compared to occupied conduction edge states (excited electrons)[1]. *H dynamics is more affected by holes*.



[1] Seems consistent with the charge injection experiments *W. Den Bower* et al., *J. Non-Cryst. Solids* 66:363–68 (1984)

Local thermal fluctuations (more local heating)

Change in the occupation of localized states (holes) gives rise to local thermal fluctuations which may spread further through H mediation.



Conclusions

- The eigenvectors near the Fermi level are mostly associated with filaments of connected long (conduction) and short (valence) bonds.
- The electron-lattice coupling is large for localized states, and for a sufficiently strained network, occupation changes can cause bond changes.

Conclusions

- Models with isolated and clustered H can be formed by allowing H to "roam free" in CRN -- it will fix the strains for you!
- Nonlocal changes accrue for changes in charge state for localized electrons/hole.
- Holes seem to stimulate more network response than electrons.

Conclusions

- We need systematics: a set of reference models with “reference defects”, and the response of the system.
- Need ways around the short time dynamics (Mousseau, ART; Parrinello scheme?).
- A complement to the Chris paradigm

learn what you can about a-Si from c-Si.