Electrons, Phonons and Topological Disorder

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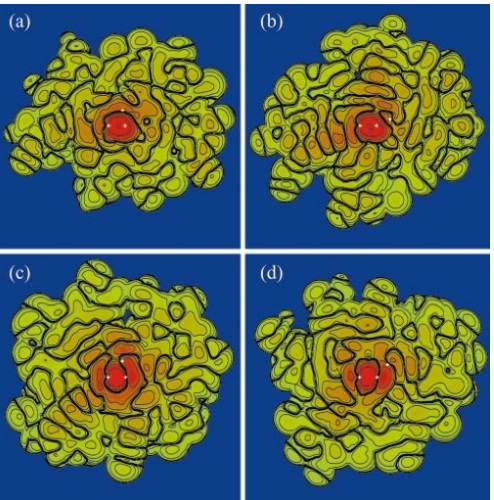
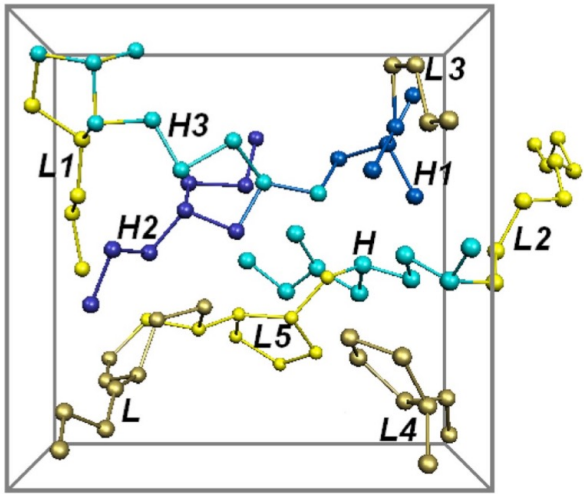
Ohio University

MRS Fall Meeting
2014





Roadmap

I. A simple picture of the Anderson transition.

II. The Urbach problem: where do exponential band tails come from?

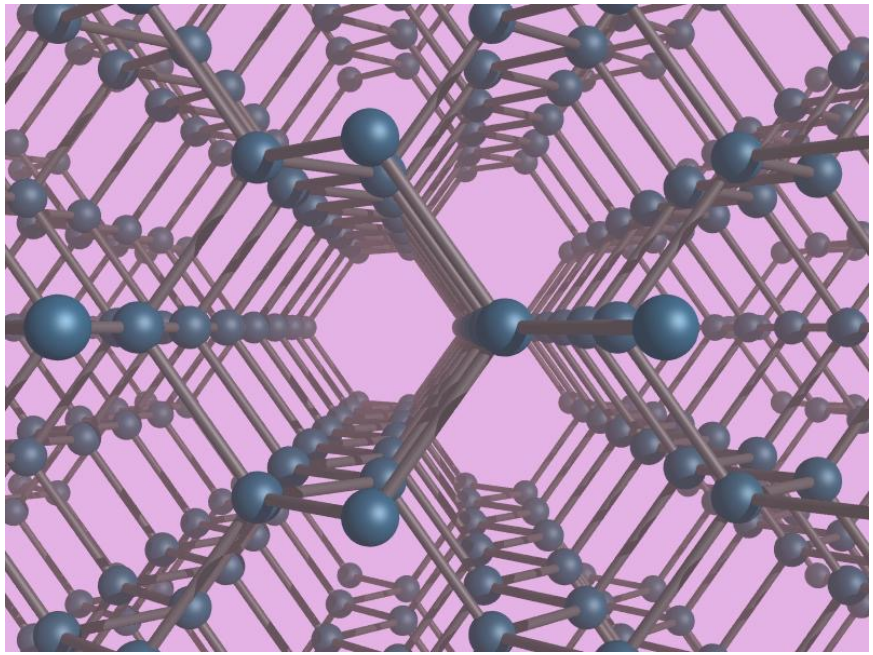
III. Non-locality of quantum mechanics in the solid state -- with disorder.

IV. The coupling to phonons.

Implement this for real materials using credible models.

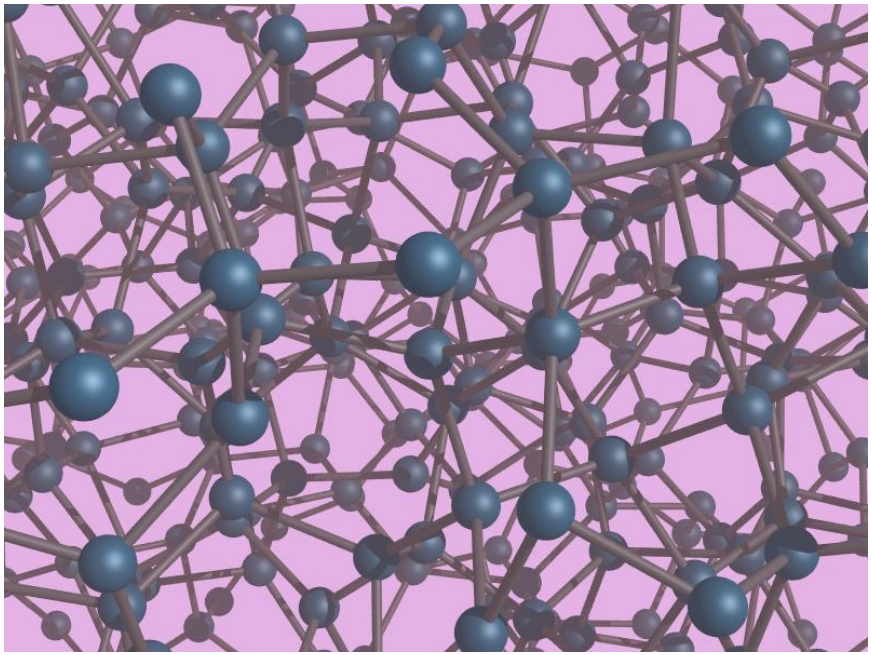
Q. How does disorder in atomic coordinates affect the electron states?

Crystalline Si (diamond)



Translational periodicity
Bloch states

Amorphous Silicon



Short-range order, no L.R.O.
k not a “good” quantum number

Models of disorder

Anderson Model (1958)

$H = \sum_I |I><I| E_I + \sum_{IJ} |I><J| S_{IJ}$

E_I are random, "diagonal" disorder. Fact -- enough variation in E_I -- all states localized!

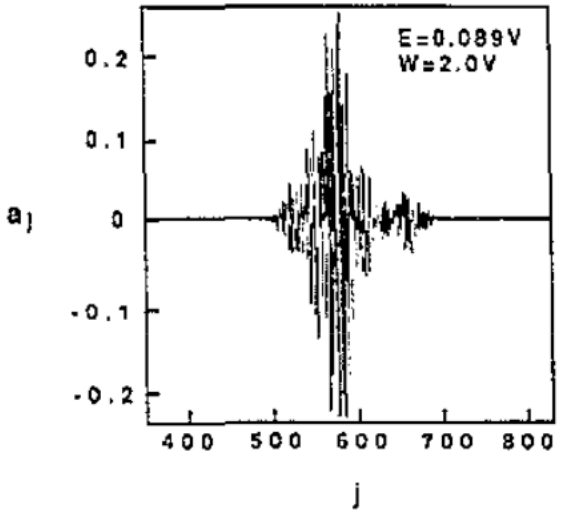
Topological (bond length/angle) disorder

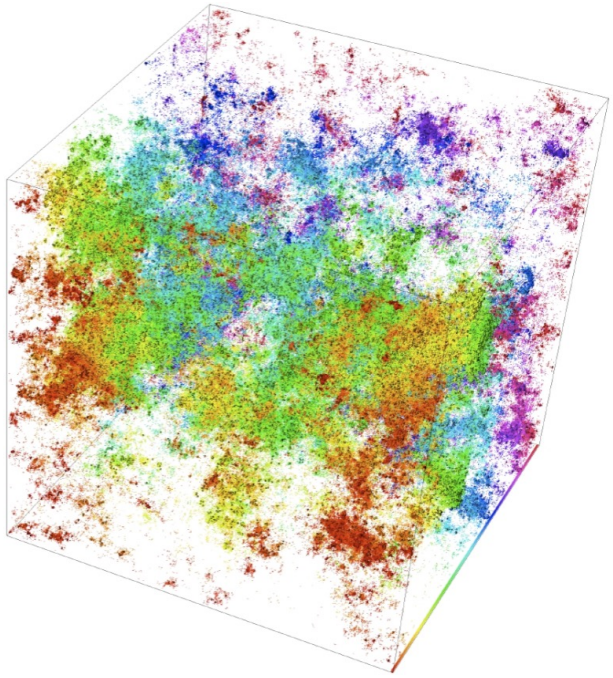
$H = \sum_I |I><I| E_I + \sum_{IJ} |I><J| S_{IJ}$

S_{IJ}: Computed from realistic model.

Anderson model: disorder uncorrelated site-to-site; our case – spatial correlations induce correlations in matrix elements.

Anderson model



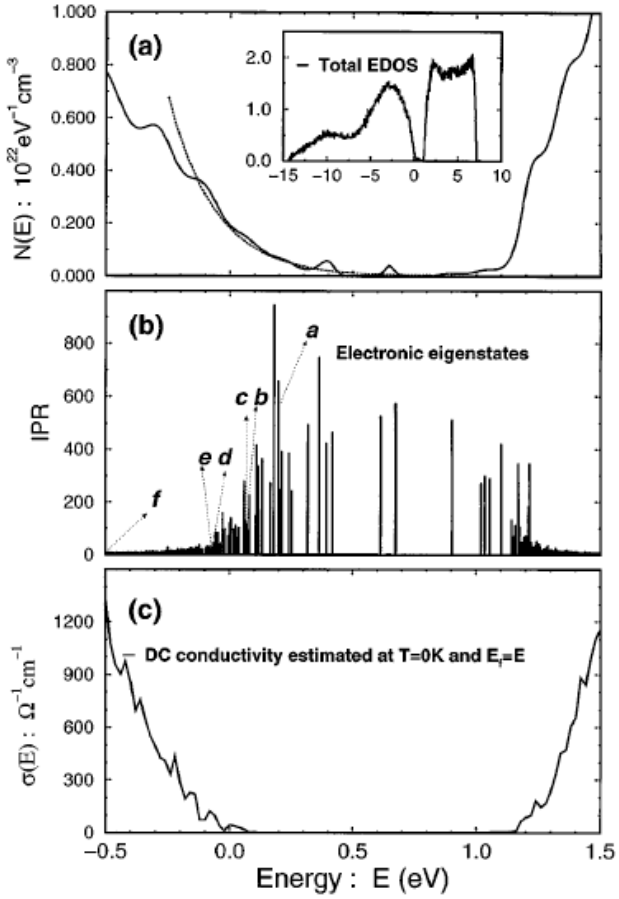


Left: A localized eigenstate in 1D (Kramer/MacKinnon)
Right: 3D critical eigenstate (15.6M sites; Roemer)

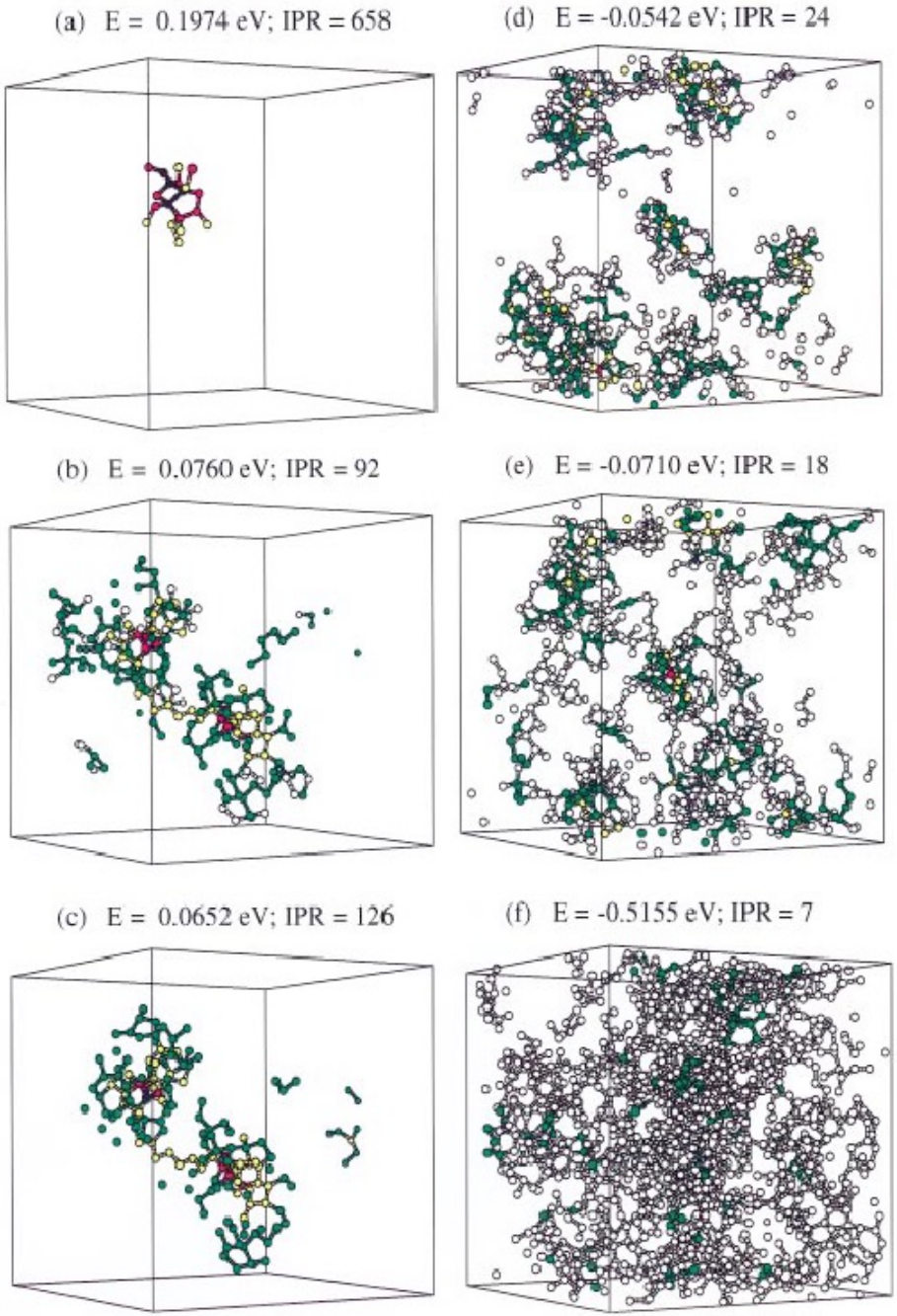
I. Approach for a real material

- Compute electronic states around the gap for big and realistic models of a-Si[1], and study the nature of the localized (midgap) to extended (in the band) transition. [4096 atoms model, periodic BC]
- Employ unholy amalgam of tight-binding, maximum entropy, shift and invert Lanczos techniques.

[1]B. Djordjevic, M. F. Thorpe and F. Wooten, PRB **52** 5685 (1995)



$|\Psi|^2$ →



Evolution of electron states in a-Si.

J-J Dong, DAD PRL **80** 1928 1998

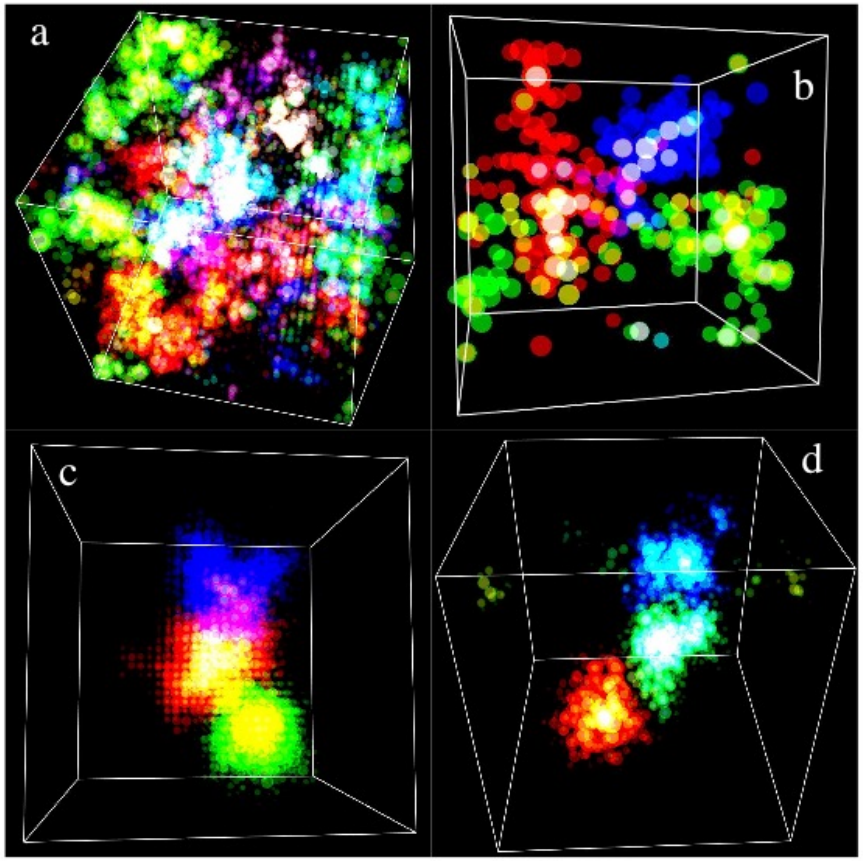
Interpretation

- Structural irregularities or defects "beyond the mean" exist.
- If "bad enough" these induce localized wave functions.
- If two such defects are spatially near and have similar energies, system eigenstates will be mixtures. "States b and c" [clue: Symmetric and anti-symmetric linear combinations of b and c yield single "islands"]
- If many such resonant defects overlap, one has "electronic connectivity". This is Mott's mobility edge.

"Resonant Cluster Proliferation" Model

Universality of island proliferation

Anderson model, W/V=16.5 (all states localized).



Vitreous silica vibrations note white centers

FCC lattice with force constants selected from uniform dist of width (W/V=2)

Vibrational evecs for 10K atom model of a-Si.

"Universality" and structure of eigenstates

- Disorder comes in many shapes and sizes.
- electrons, Anderson models (diagonal and off-diagonal); "real" disorder from topologically disordered network.
- vibrations "Substitutional"; Force constant disorder on a FCC lattice; Topological disorder (a-silica) with long-range (Coulomb) interactions; (a-Si)10,000 atom

The qualitative nature of the localized-extended transition is similar for all these systems.

Ludlam, Taraskin, Elliott, DAD – JPCM **17** L321 (2005).

Do the correlations in matrix elements matter?

- The Anderson model gets all the qualitative features right: islands, resonant mixing *etc.* around spectral gaps.
- But *not* the fine but important details around the band edges.

Yes – the correlations matter.

II. The Urbach tail problem

- Urbach[1] noted exponential (not Gaussian) tails in optical absorption for impure crystals in 1953:

$$\alpha(\omega) \propto exp[(\hbar\omega - \hbar\omega_0)/E_0]$$

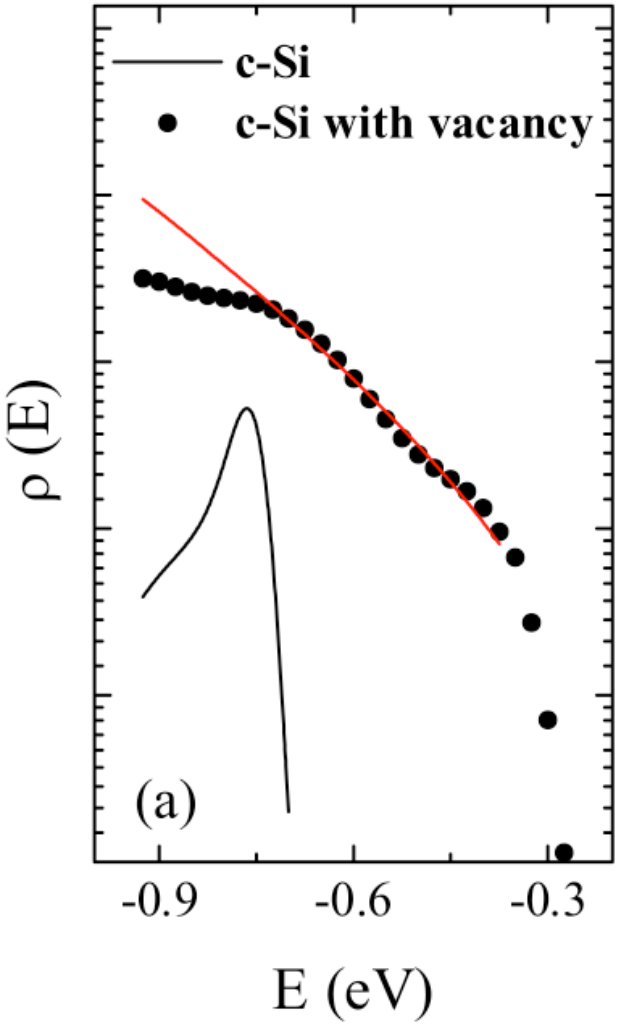
ω: photon frequency, ω_0 and E_0 fitting parameters

- It is ubiquitous (particularly in systems with disorder).
- Venerable problem – various ideas: Halperin-Lax, Morrell Cohen et al, Dow-Redfield... Very different models.
- This has been carefully studied in amorphous Si. Exponential tails measured separately for each band edge[2].

[1]F. Urbach, PR **92** 1324 (1953)
[2]S. Aljishi *et al*., PRL **64** 2811 (1990)

Preliminary: Defective xtal and ion-bombarded diamond Si

- Experiment[1]: ion-damaged diamond exhibits an exponential tail.
- Simulation[2]: SIESTA relaxed di-vacancy in 512-atom cell forms exponential tail.
- Relaxing di-vacancy yields strain field involving many atoms. The beginning of the Urbach tail?



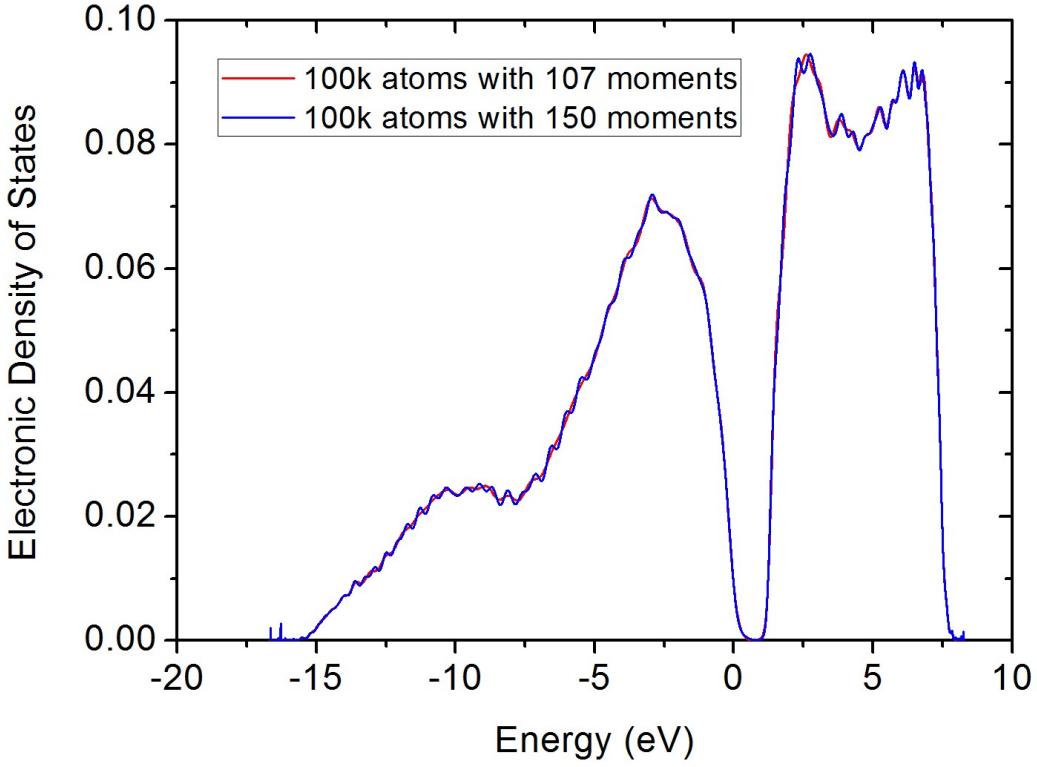
[1]S. Sundari, Nuc. Inst. Meth. B **215** 157 (2004)
[2]Y. Pan, F. Inam, M. Zhang, DAD, PRL **100** 206403 (2008)

Density of states: large amorphous Si model

- Model: Barkema and Mousseau WWW-type: 100,000 atoms. Excellent RDF, fourfold, tetrahedral with little strain.
- Hamiltonian: Kwon *et al*. orthogonal tight-binding model, maximum entropy tricks to compute the DOS (ask me…)

G. Barkema and N Mousseau, PRB **62** 4985 (2000)
DAD and O. F. Sankey, PRL **70** 3631 (1993); DAD EPJB **68** 1 (2009); K. Bandypoadhyay *et al*, PRE **71** 057701 (2005)
I. Kwon *et al*, PRB **49** 7242 (1994)

Density of states: reconstruction from moments

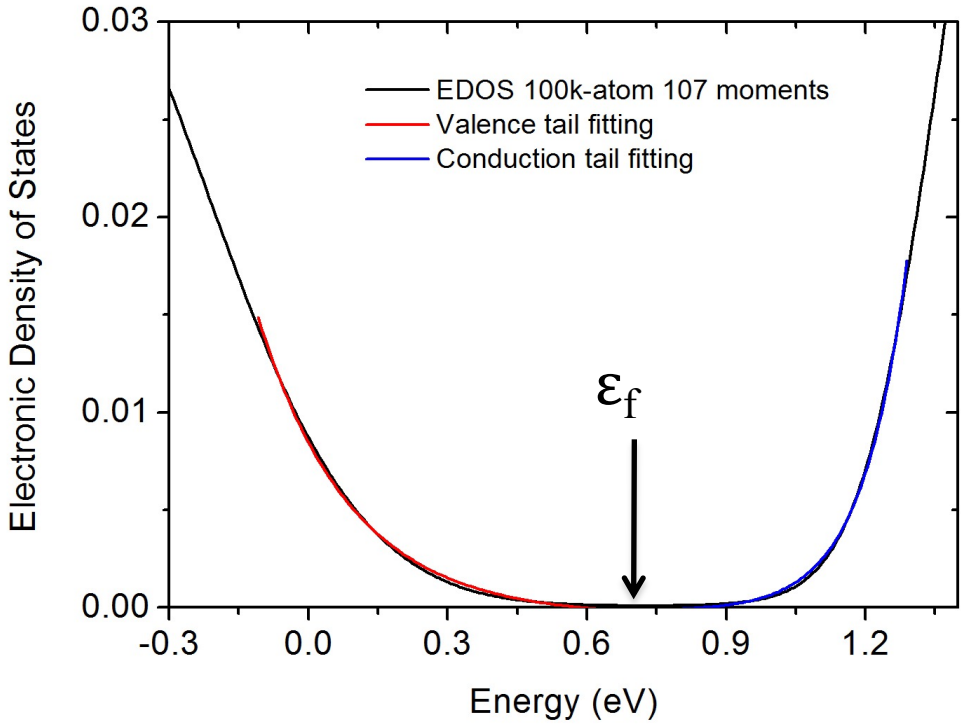


Maxent form:
find Λ_i to match moments

$$\rho(E) = exp(-\sum_{i=0}^{107} \Lambda_i E^i)$$

E. T. Jaynes, *Probability Theory: The Logic of Science*, CUP (2003); DAD and O. F. Sankey, PRL **70** 3631 (1993).

Result: exponential tails in a-Si



$$\rho(E) \propto exp(-|E - E_b|/E_U)$$

E_U=200 meV (valence)

E_U=96 meV (conduction)

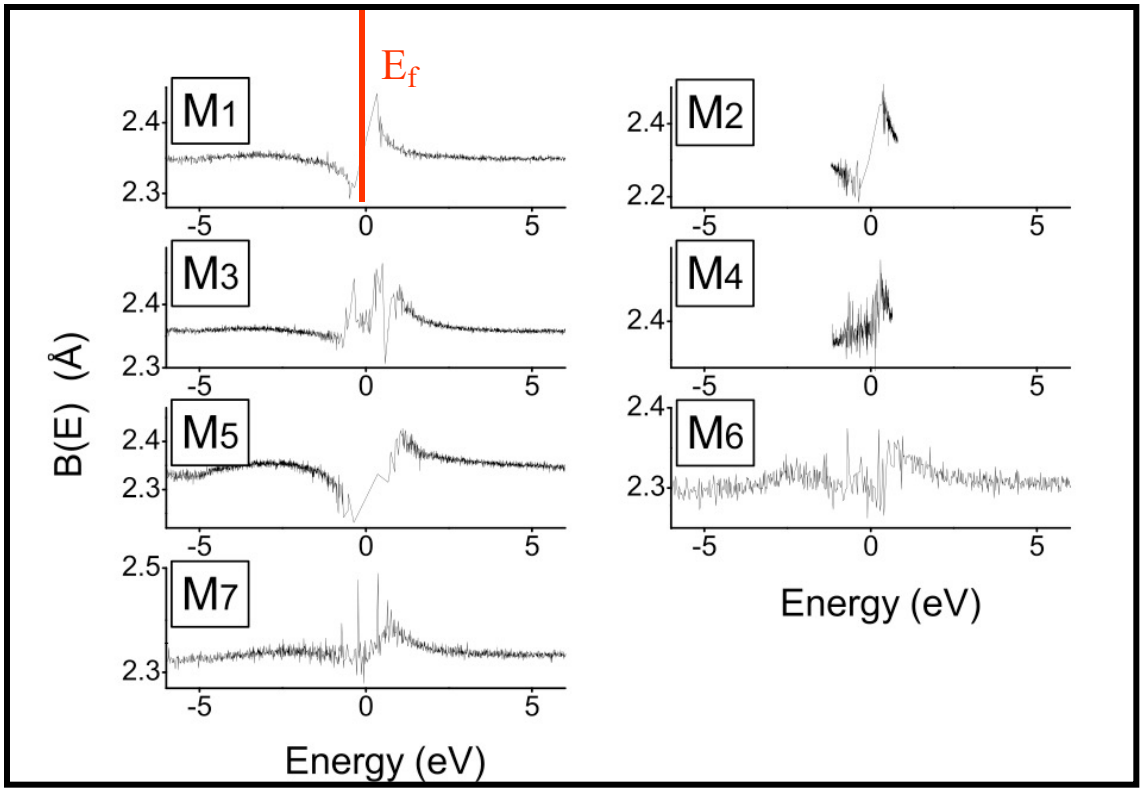
Discussion

- The models include whatever structures “cause” the exponential tails.
  - conduction tail: due to 1-D filaments of long bonds.
  - valence tail: due to 3-D clusters of short bonds ‘nucleated’ by a particularly short bond.

Y. Pan, F. Inam, M. Zhang and DAD, PRL **100** 206403 (2008).

Tail states

Bondlength decomposition as function of energy

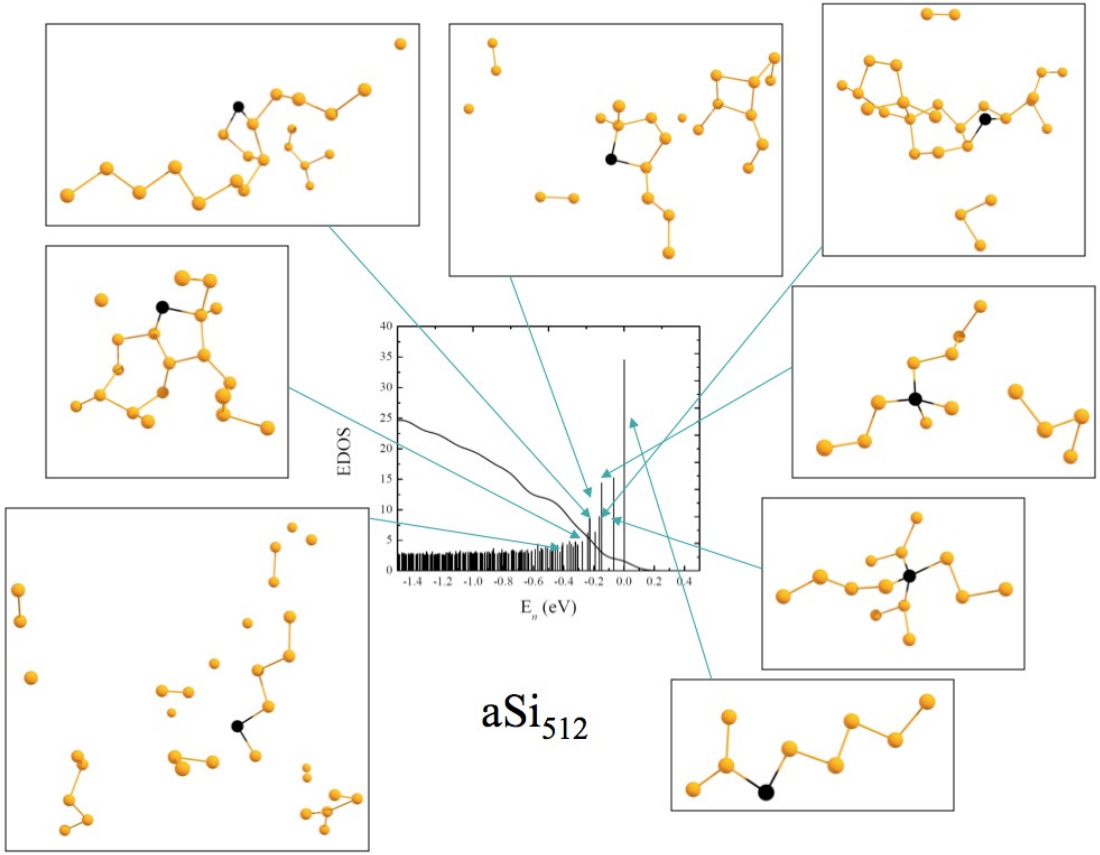


M_1, M_2 – WWW (DTW)
M_3-MD (Feldman)
M_4-ART (Mousseau)
M_5-WWW+xtal
M_6,M_7 – RMC (allowing defects)

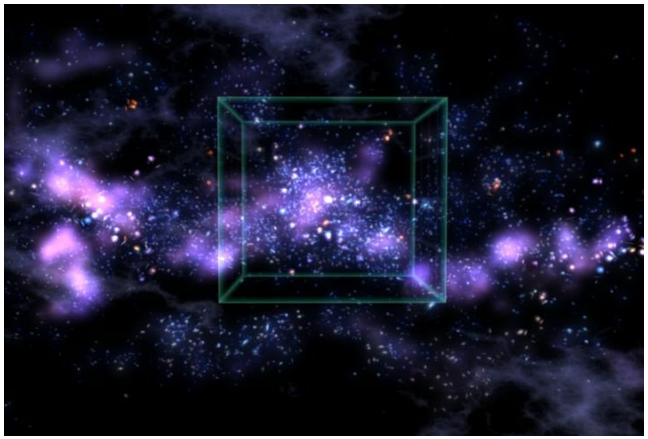
Phys. Rev. B **58** 15624 (1998)
J. Non. Cryst. Sol. **354** 3480 (2008)

Messages: 1) valence tail from short; 2) conduction from long; 3) Defects add 'noise' – but the pattern is evident nevertheless; 4) Note the symmetry in B(E) about E_f, especially for M_1.

Blobs and filaments: valence states



Valence tail: connected blobs and filaments

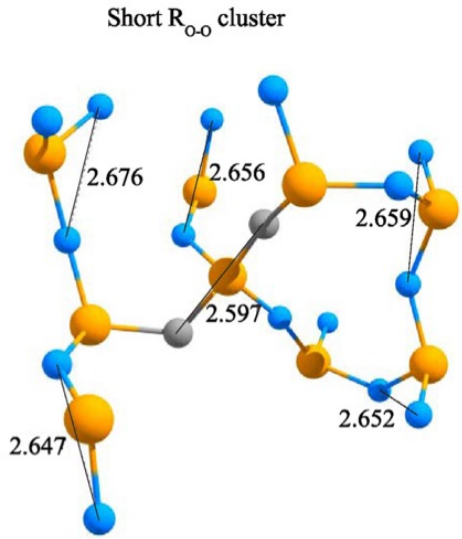


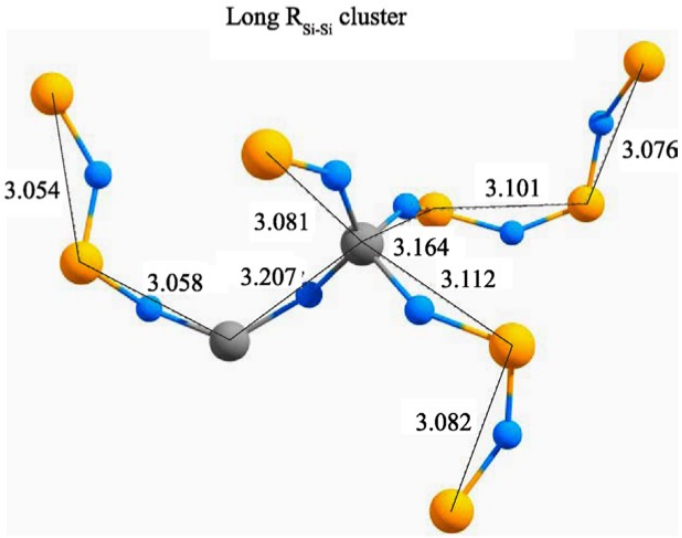
Other *blobs and filaments*: Lyman α emisson from a giant galaxy 'string'. Paul Francis, ANU, 2004

Blobs and filaments in solids, not space:
J. Dong & DAD PRL **80** 1928 (1998)
J. Ludlam, S. R. Elliott, S. N. Taraskin & DAD JPCM **17** L321 (2005)

a-Silica

- Silica tails: small $\theta_{O\text{-}Si\text{-}O}$ (valence), large $\theta_{Si\text{-}O\text{-}Si}$ (conduction).





F. Inam, J. Lewis, DAD PSS(a) **207** 599 (2010)

Conclusion: Urbach tails

- Shorter bond 'nuclei' create clusters of connected short bonds; local densification. Long bonds, wispy filaments.
- ***Short bonds*: valence tail**, ***long bonds*: conduction tail.**
- Our models are too small to accurately compute fractal dimension D but we surely have:

  Filaments: D near 1 on the conduction side

  Clusters: D significantly higher than for the valence side

  We link such electronic information to the connectivity/structure of the network. D is unknown for a real material – and varies asymmetrically about E_f.. [D~1.3 for Anderson model.]
- Some indication of greater generality: silica

III. Locality of QM in disordered solid state

Even for disordered system: almost all eigenstates fill space. Looks like the force on atom at **R** requires information from everywhere!

$$F_{bs}^{\mathbf{R}} = 2 \sum_{n \ occ} \langle \psi_n | - \nabla_{\mathbf{R}} H | \psi_n \rangle$$

[Here, ψ_n is a Kohn-Sham orbital.]

Can perturbing the solid 1*m* away from **R** really change the force on at **R**??? (**No**! Boys, Kohn, Vanderbilt, Daw...)

Density matrix: gauge of electronic nonlocality

eigenstates

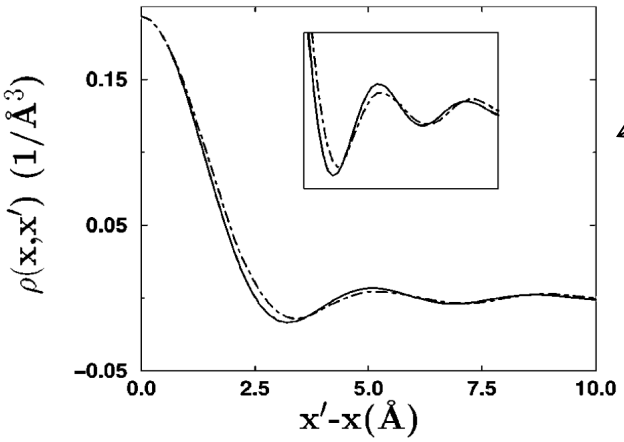
$$\rho(\mathbf{x},\mathbf{x}') = 2 \sum_{n}^{\text{occ}} \psi_n^*(\mathbf{x})\,\psi_n(\mathbf{x}')$$

W. Kohn: Density matrix ρ is localized by destructive wave-mechanical interference. ***Principle of Nearsightedness***

One might suppose that *destructive wave-mechanical interference* should be influenced by structural disorder. Is it?

The decay of the density matrix is fundamental attribute of the material (and structure).

Example: Aluminum



$$\rho(\mathbf{x},\mathbf{x}') = 2(2\pi)^{-3}\int_{\mathbf{k}<\mathbf{k}_F} d^3k e^{-i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')}$$

$$= 3n[\sin(\zeta) - \zeta\cos(\zeta)]/\zeta^3,$$

$\zeta = k_f|x\text{-}x'|$

n: density of electron gas

Kohn-Sham

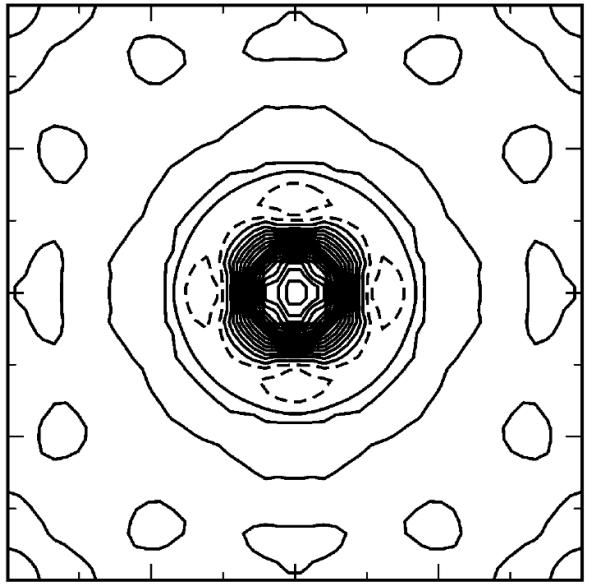


FIG. 4. Contour plot of the real-space density matrix for Al calculated in the {100} plane for the conventional cubic unit cell (the x-y axes are parallel to the bonds).

S. N. Taraskin *et al.*, PRB **66** 233101 (2002)

Metal: power law decay. Free electron gas gives similar DM to DFT! Gibbs' ringing* from cutoff at Fermi surface.

*Published by Henry Wilbraham (1848), *On a certain periodic function*, The Cambridge and Dublin Mathematical Journal **3**: 198–201, Trinity College, when 22 years old, 50 years before Gibbs!

Decay of density matrix in insulators: analytic approach

Start with centrosymmetric n.n. tight-binding Hamiltonian

$$\hat{\mathbf{H}} = \sum_{i\mu} \varepsilon_\mu |i\mu\rangle\langle i\mu| + \sum_{i\mu, j(i)\mu'} t_{\mu\mu'} |i\mu\rangle\langle j\mu'| .$$

Two orbitals per site, bonding and antibonding, SC lattice.

Density matrix is integral over Brillouin zone:

$$\rho(\mathbf{r}_{ij}) = \frac{-1}{2(2\pi)^D} \int \cdots \int_{-\pi}^{\pi} d\mathbf{k} \, \frac{e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} S_{\mathbf{k}}}{(A_{\mathbf{k}}^2 + S_{\mathbf{k}}^2)^{1/2}}$$

S(k) is structure factor, A(k) depends on S and tight binding parameters.

D.M. asymptotics (cont'd)

$$\rho_{\nu_\alpha} = \frac{(-1)^{\overline{\nu}}}{(4A)^{2\overline{\nu}+1}} \sum_{k=0}^{\infty} (-1)^k \left[\frac{(2k')!}{(4A)^k (k')!} \right]^2 (2k' + 1)\Sigma_D$$

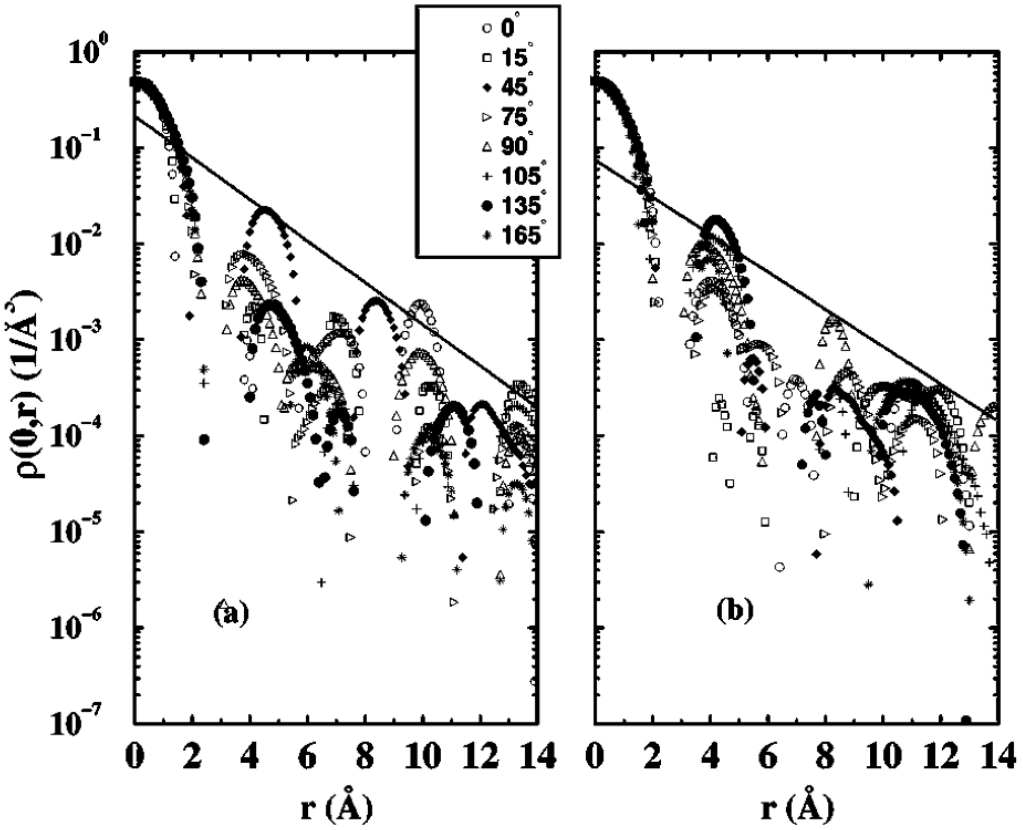
Σ is a (known) sum, depending on dimensionality D=1,2,3

Sum the series, use Stirling approximation, in 3D get (for example):

$$\rho_{\nu_\alpha} \simeq (-1)^{\overline{\nu}} \sqrt{\frac{\nu_+}{2\pi \nu_x \nu_y}} \exp\left[-\nu_+ \left(1 + \frac{\nu_-}{2\nu_+} \ln(\nu_x/\nu_y) \right) \right]$$
$$\times J_{\nu_z}\left[\frac{\nu_+}{A} \right] J_{\nu_+}\left[\frac{\nu_+^2}{\sqrt{\nu_x \nu_y} A} \right], \qquad (7)$$

2d, 3d: S. Taraskin, DAD, Elliott PRL **88** 196405 (2002); also 1d: L. He and D. Vanderbilt, PRL **86**, 5341 (2001).

Realistic calculations (c-Si and a-Si): DFT



The same exponential decay, crystal or amorphous!

X. Zhang and DAD, PRB **63** 233109 (2001).

Wannier functions

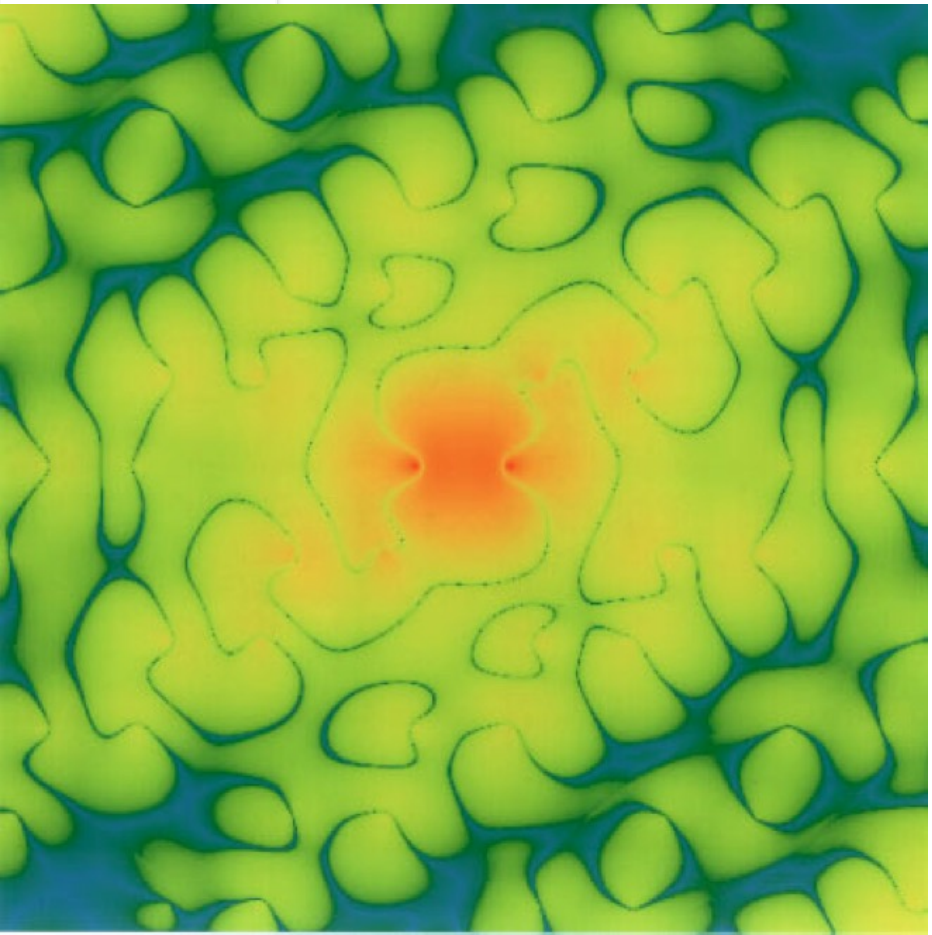
- Wannier functions: unitary transformations of eigenstates localized in real space.
- Not unique, *but* Vanderbilt showed how to compute maximally-localized Wannier functions[1].
- Long range decay of these is similar for c-Si and a-Si, and similar to decay of density matrix.
- We compute with an O(N) projection method, results much like MLWFs.

[1]D. Vanderbilt and coworkers "**Maximally-localized WF**", N. Marzari *et al*, RMP **84** 1419 (2012)

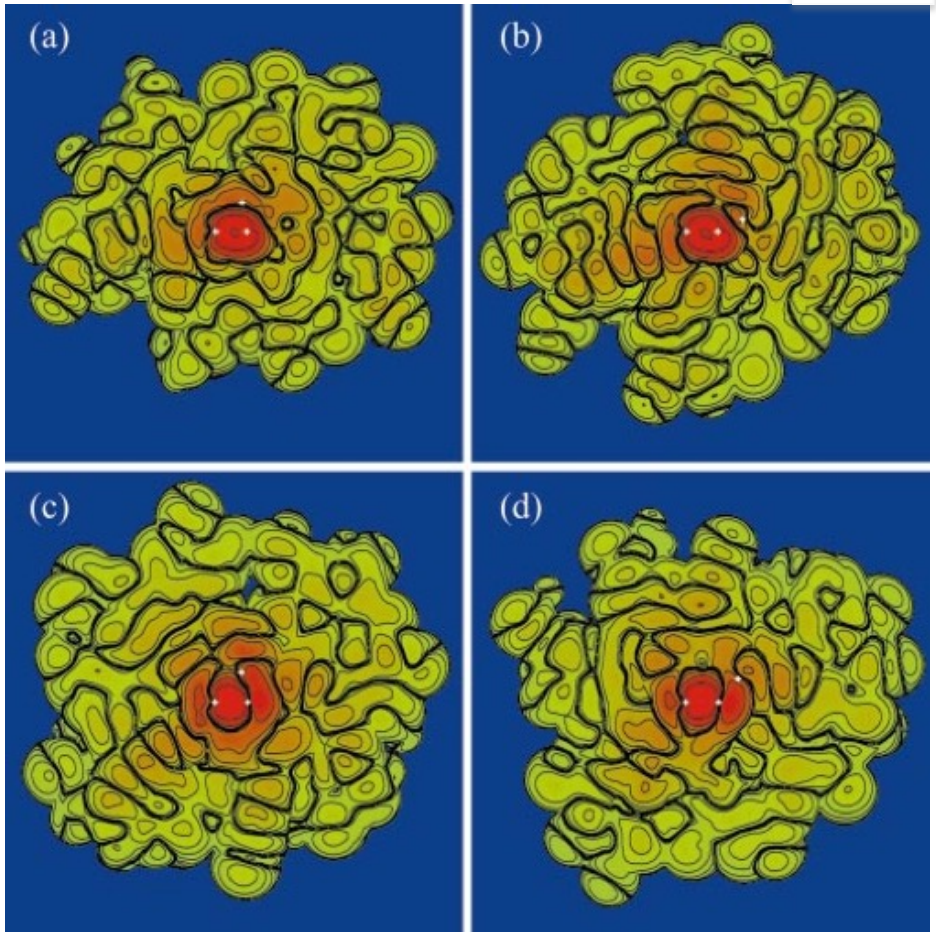
Wannier functions for disordered systems

DAD Eur. Phys. J B 68 1 (2009)

Diamond



a-Si



Conclusion: Locality

We quantify Kohn's Principle:

(1) Analytically for two-band insulator

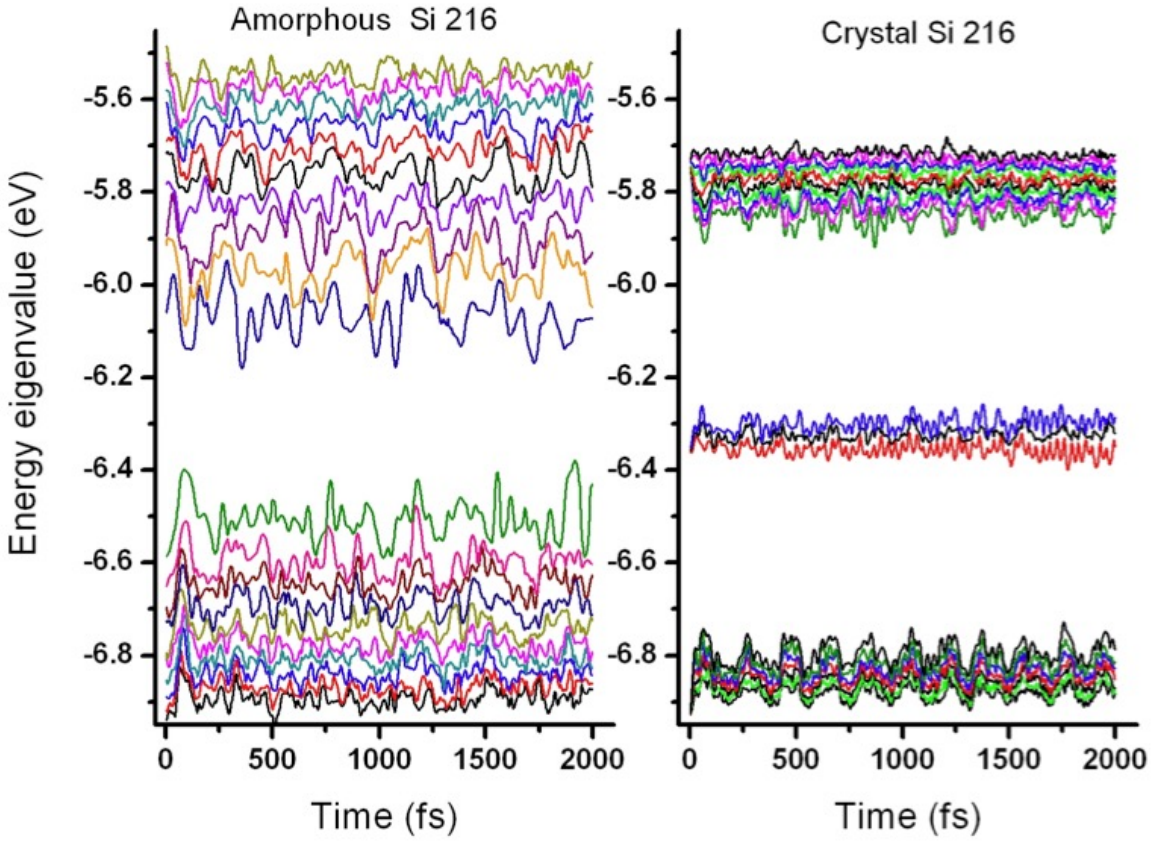
(2) By direct calculation of ρ with Kohn-Sham orbitals for metals, crystalline and amorphous semiconductors. Also Wannier functions from projection.

(3) Topological disorder makes little qualitative difference, at least for a-Si (and SiO_2).

IV. But what of *Localized* Electrons + Phonons

- The electron-phonon coupling gauges how the electron energies/states change with atomic deformation.
- Phonon effects near the Fermi level: key to transport, device applications, theory of localization.
- We begin with a simple simulation….

Thermal fluctuations of the Kohn-Sham eigenvalues



T=300K, 216 atoms, Γ point

States near gap fluctuate by *tenths* of eV >> kT !

Sensitivity of electron energy to particular phonon

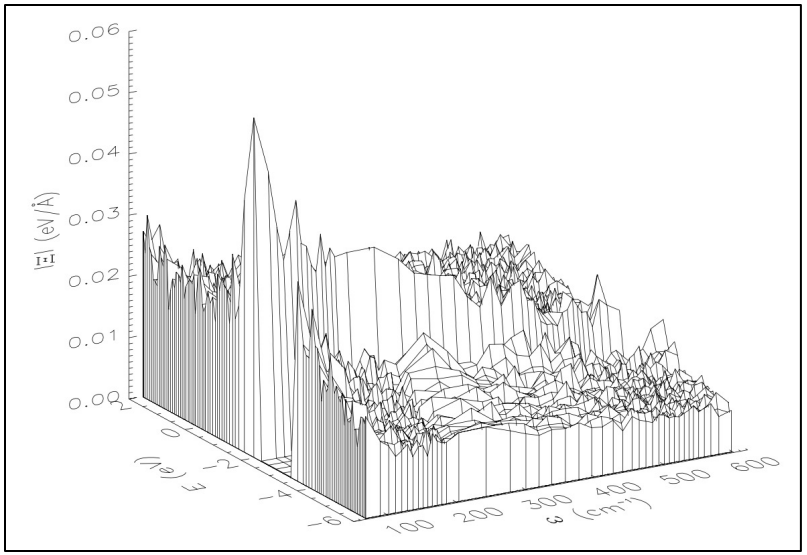
- Hellmann-Feynman theorem and harmonic approximation with classical lattice dynamics leads easily to fluctuations in electron energy eigenvalue $\langle \delta\lambda^2 \rangle$:

$$\langle \delta\lambda_n^2 \rangle = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau dt\, \delta\lambda_n^2(t) \approx \left(\frac{3k_B T}{2M} \right) \sum_{\omega=1}^{3N} \frac{\Xi_n^2(\omega)}{\omega^2},$$

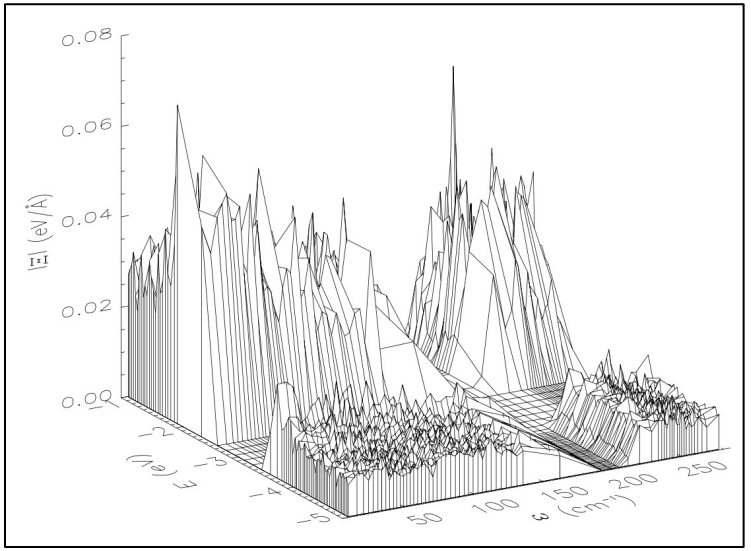
$$\Xi_n(\omega) = \sum_{\alpha=1}^{3N} \langle \psi_n | \frac{\partial \mathbf{H}}{\partial \mathbf{R}_\alpha} | \psi_n \rangle\, \chi_\alpha(\omega).$$

We call Ξ the electron-phonon coupling

E-P coupling: a-Si, a-Se



Si



Se

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

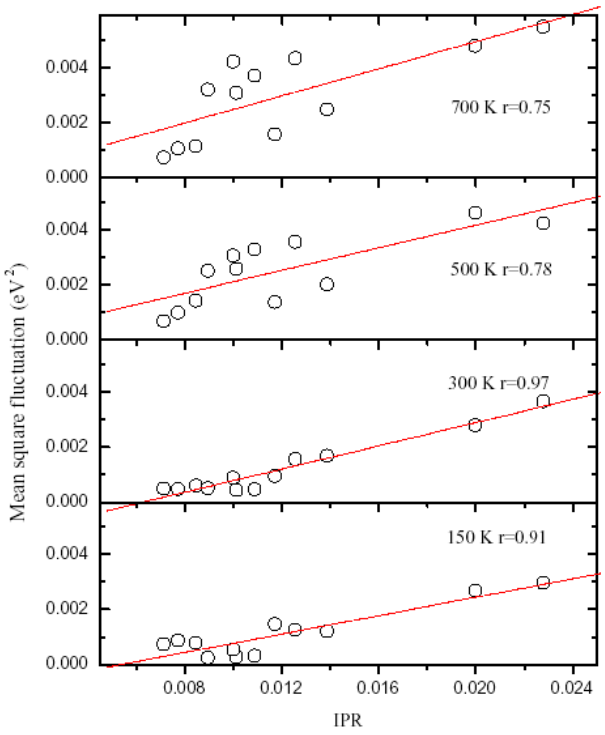
Couple electron n (energy E) and phonon ω

R. Atta-Fynn, P. Biswas, DAD *Electron-phonon coupling is large for localized states*, PRB **69** 245204 (2004)

Correlation between localization and thermal fluctuation from MD

$\langle \delta\lambda^2 \rangle$

(T>0 property)



700K

500K

300K

150K

Fits analytic result for low T

Localization (T=0 property)

Interpretation

1. Large e-p coupling for localized states near the gap. *Localization amplifies e-p coupling.*

2. For localized states, simple algebra[1] leads to the conclusion that:

a) $\Xi_n(\omega)^2$ [for eigenvalue n] ~ IPR [n]

b) $\langle \delta\lambda^2 \rangle \sim$ IPR

IPR = inverse participation ration; measure of localization

[1]Atta-Fynn, Biswas and DAD, PRB **69** 254204 (2004)

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