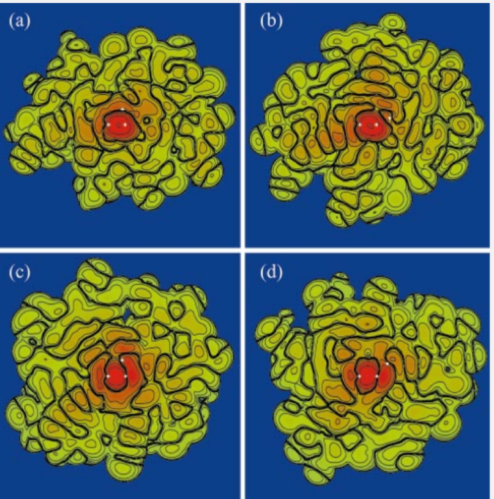
ELECTRONS AND PHONONS: CALCULATIONS IN DISORDERED MATERIALS

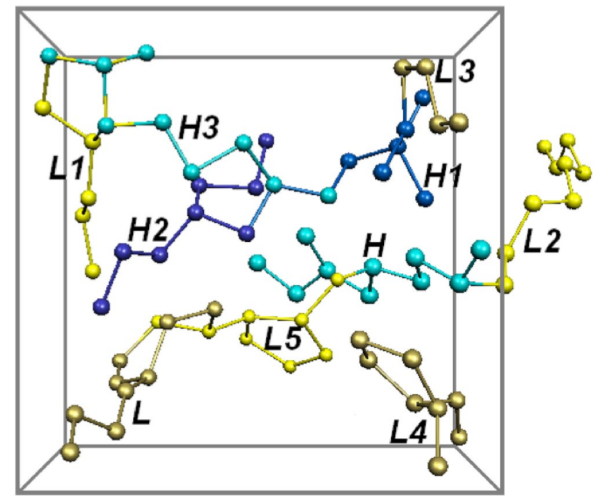
David Drabold

Ohio University



Petra

2018



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.

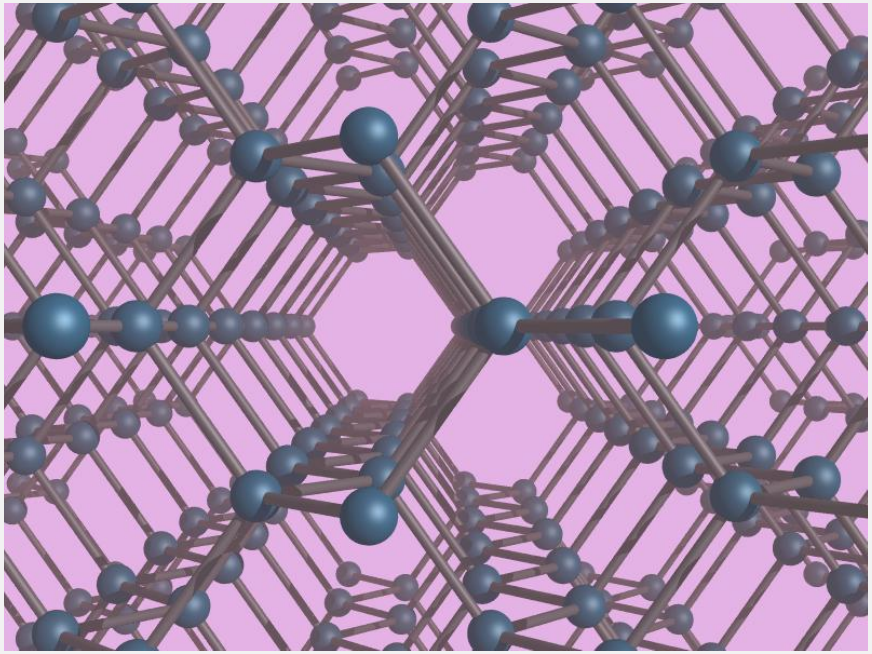
V. Materials by Design: an attempt at engineering the optical gap.

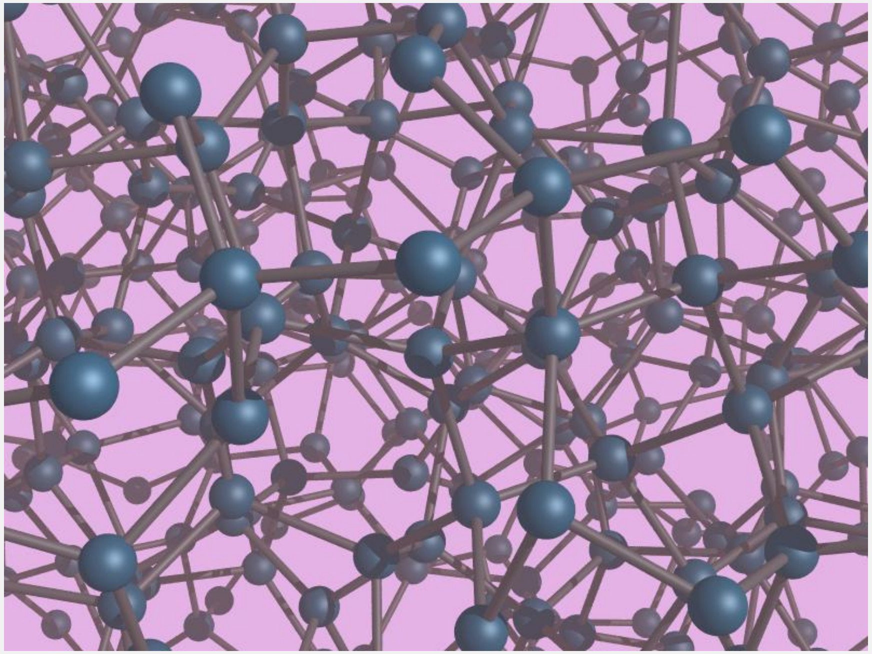
VI. Space-projected conductivity

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

Crystalline Si (diamond)

Amorphous Silicon

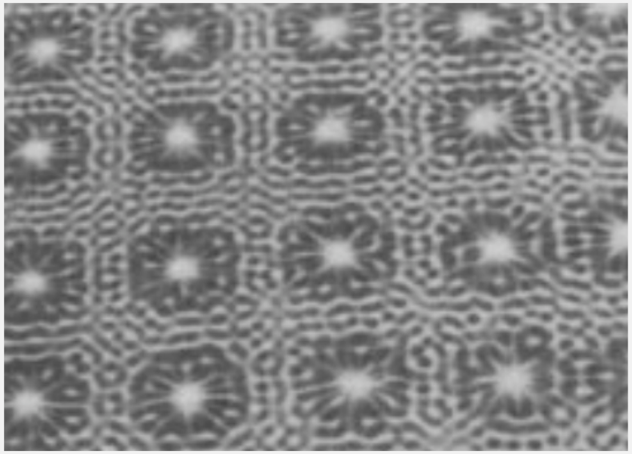


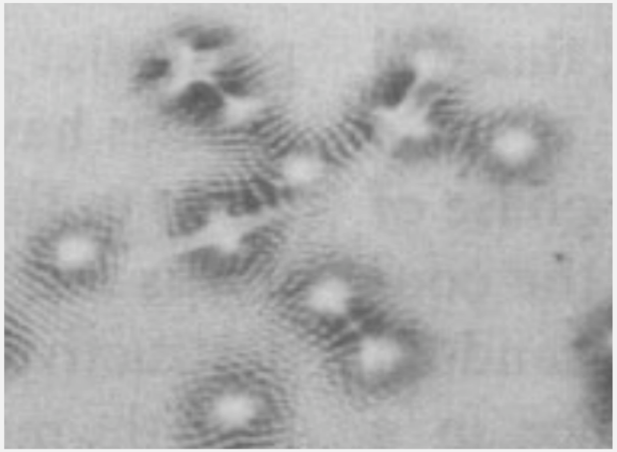


Translational periodicity
Bloch states

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

DISORDER + WAVES = LOCALIZATION





Water waves with obstacles; left periodic obstacles, commensurate frequency to yield "Bragg reflection", note that pattern is extended in space. Right: disordered obstacles, standing waves – **localization!**

If its true for water, why not electrons too?!

Lindelof *et al.* 1996

Models of disorder

Anderson Model (1958)
$H = \sum_I |I\rangle\langle I| E_I + \sum_{IJ} |I\rangle\langle J| S_{IJ}$

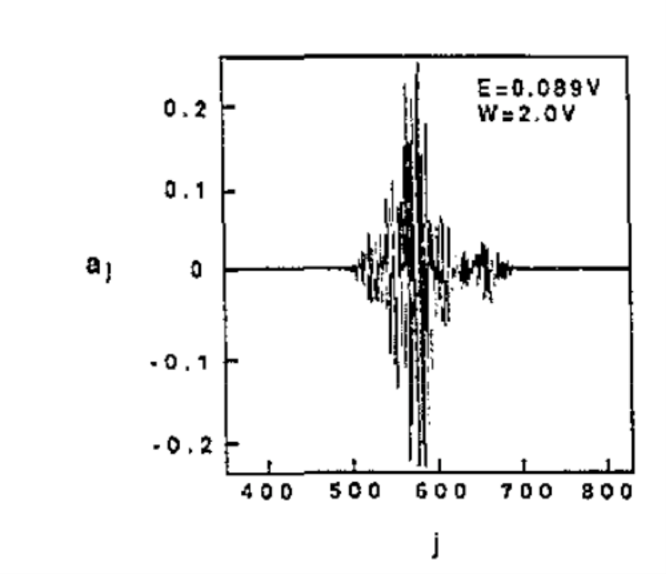
E_I are random, "diagonal" disorder. Fact -- enough variation in E_I -- all states localized!

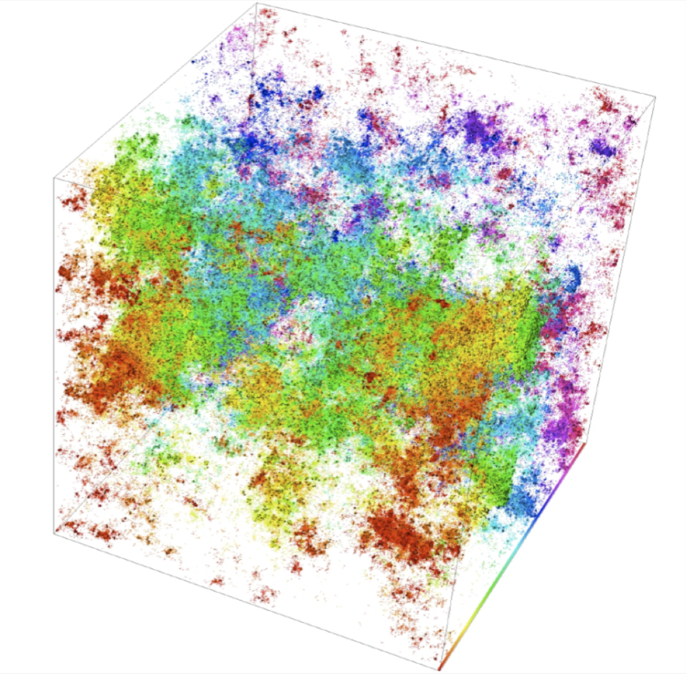
Topological (bond length/angle) disorder
$H = \sum_I |I\rangle\langle I| E_I + \sum_{IJ} |I\rangle\langle J| S_{IJ}$

S_{IJ}: *Computed from realistic model.*

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

ANDERSON MODEL



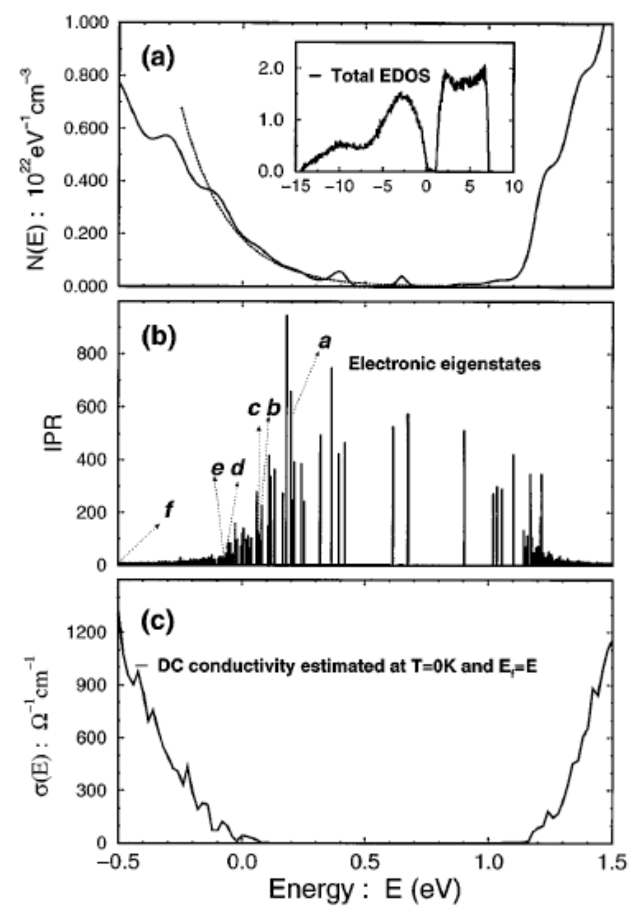


Left: A localized eigenstate in 1D (Kramer/MacKinnon)
Right: 3D critical eigenstate (15.6M sites; Roemer)

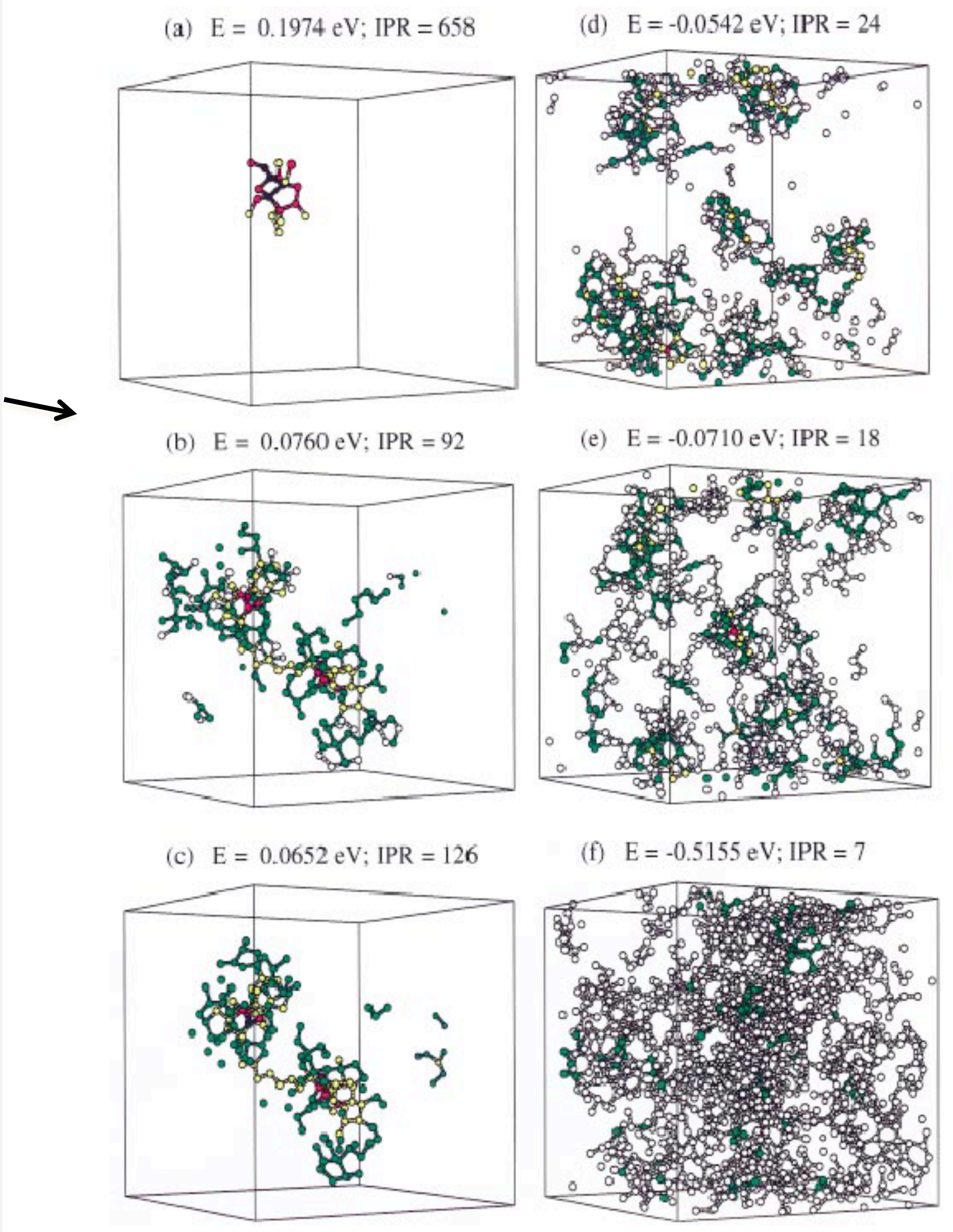
APPROACH FOR A REAL MATERIAL

- 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 amalgam of tight-binding, maximum entropy, shift and invert Lanczos techniques.

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



$|\Psi|^2 \longrightarrow$



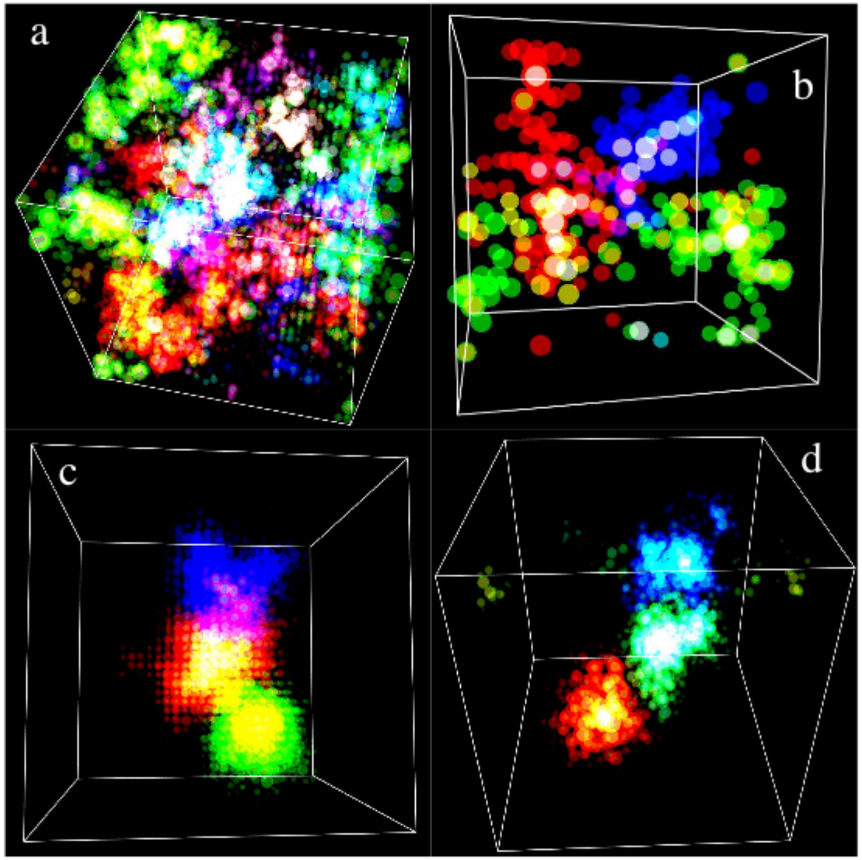
Evolution of electron states in a-Si. J-J Dong, DAD PRL **80** 1928 1998

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.

JPCM **17** L321 (2005)

"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

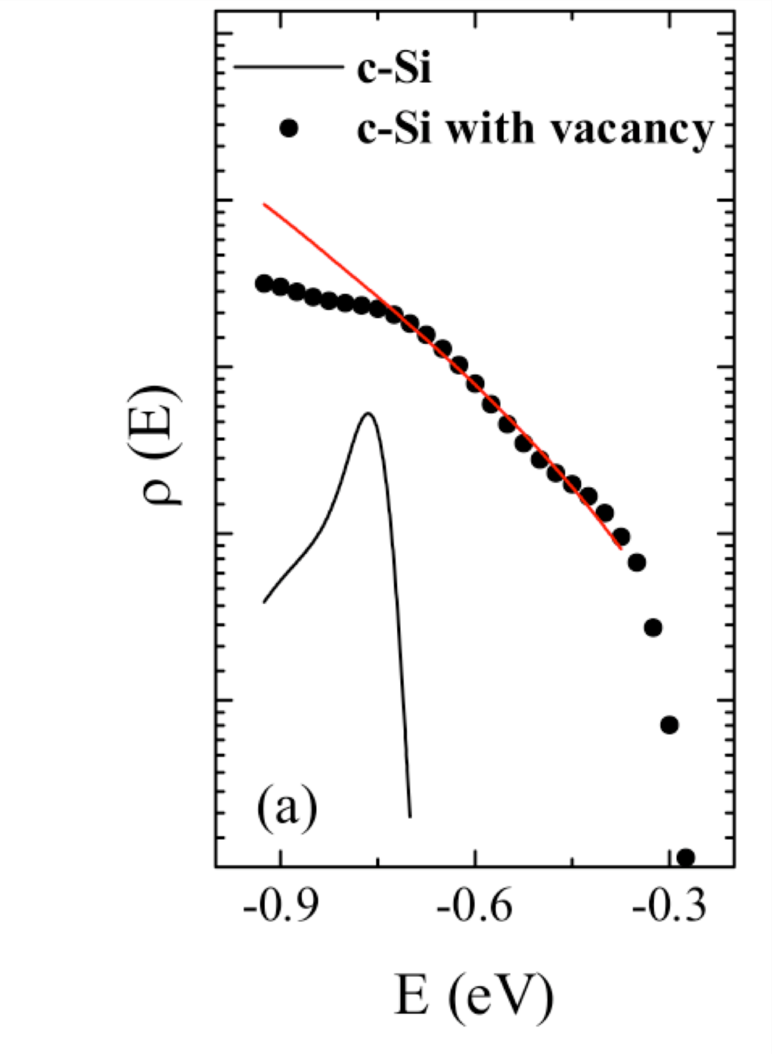
- It is ubiquitous (particularly in systems with disorder).
- Venerable problem – various ideas: Halperin-Lax, Morrell Cohen *et al*, Dow-Redfield... *Very different models*.
- This has been carefully studied in amorphous Si. Exponential tails measured separately *for each band edge*[2].

[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)

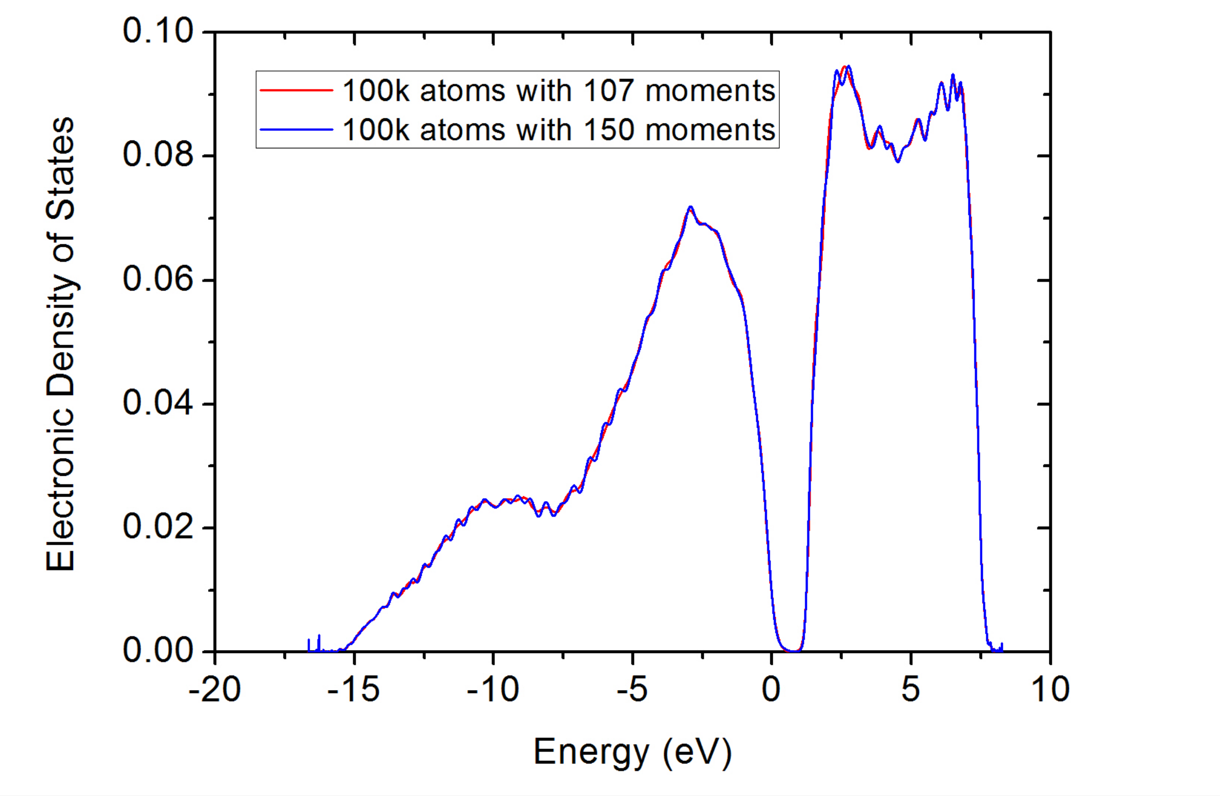
[2] Y. Pan, F. Inam, M. Zhang, DAD, PRL **100** 206403 (2008)

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



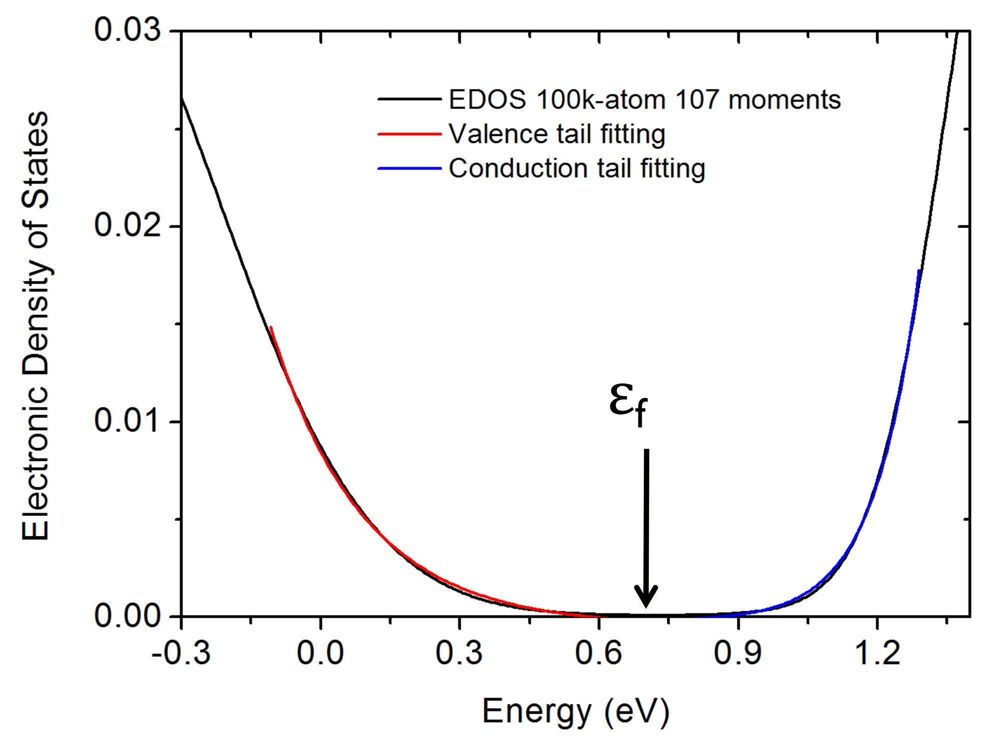
Maxent form:

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.

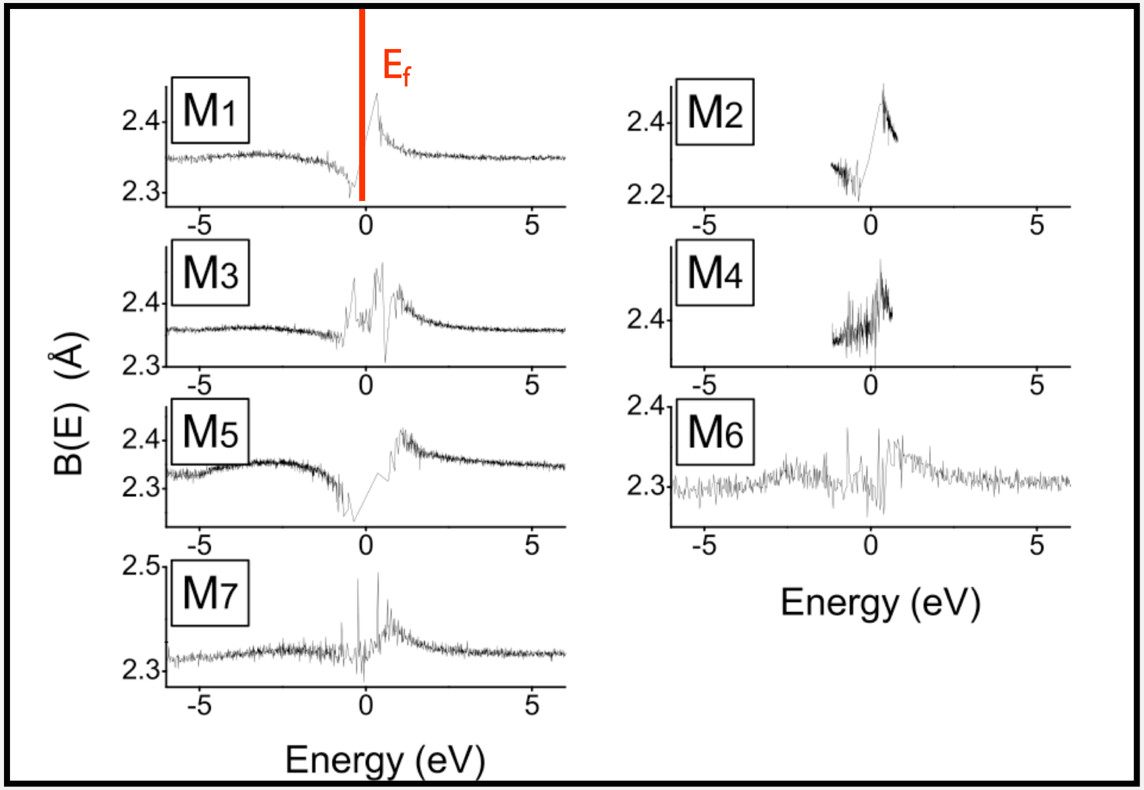
○ conduction tail: due to 1-D filaments of long bonds.

○ 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

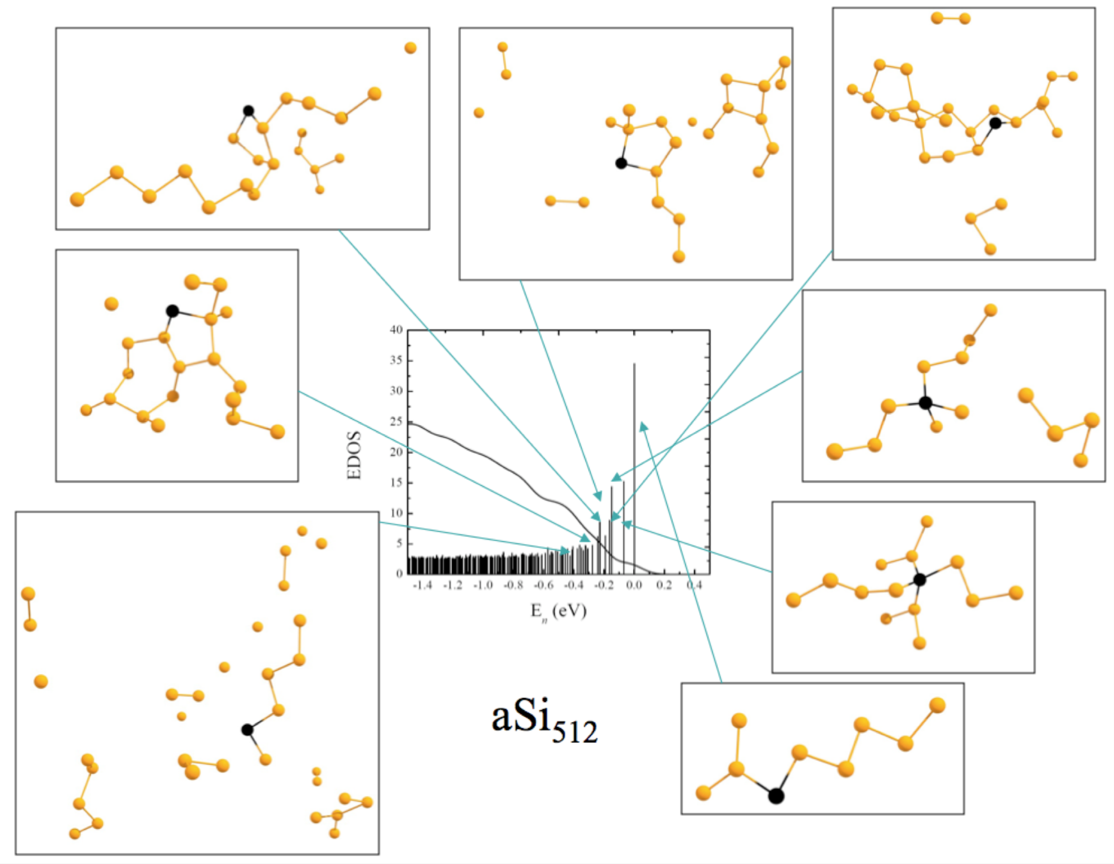


M_1, M_2 – WWW (DTW)
M_3-MD (Feldman)
M_4-ART (Mousseau)
M_5-WWW+xtal
M_6,M_7 – RMC (allowing defects)

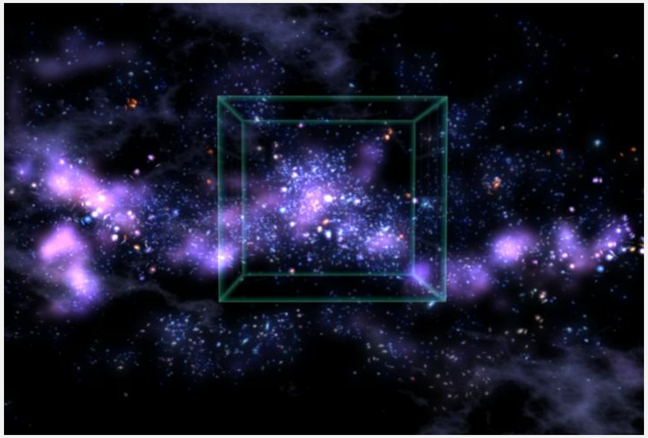
Phys. Rev. B 58 15624 (1998)
J. Non. Cryst. Sol. 354 3480 (2008)

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

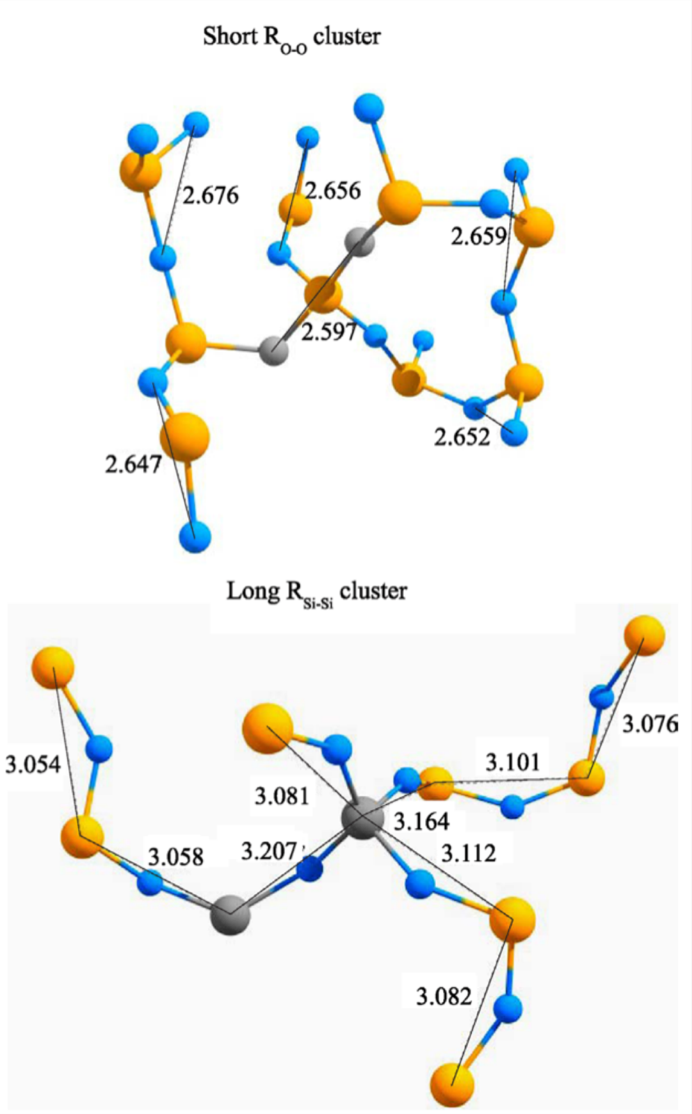


Other blobs and filaments: Lyman α emisson from a giant galaxy ‘string’. Paul Francis, ANU, 2004

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)

AMORPHOUS SILICA

- Silica tails: small $\theta_{\text{O-Si-O}}$ (valence), large $\theta_{\text{Si-O-Si}}$ (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 1m away from **R** really change the force on at **R**??? (No! *Boys, Kohn, Vanderbilt, Daw…*)

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

DENSITY MATRIX: GAUGE OF ELECTRONIC NONLOCALITY

eigenstates

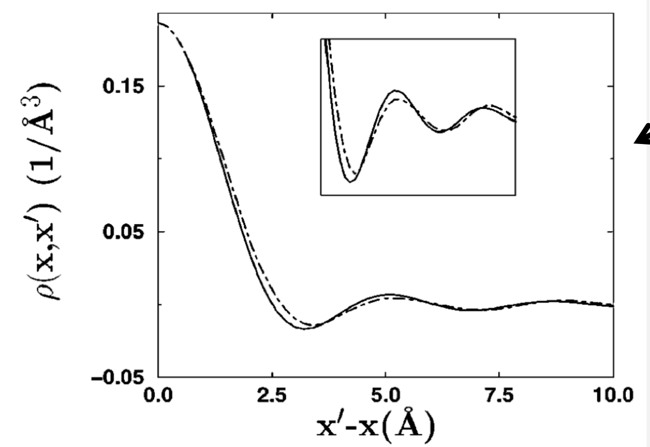
$$\rho(\mathbf{x},\mathbf{x}')=2\sum_{n\ \mathrm{occ}}\psi_n^*(\mathbf{x})\,\psi_n(\mathbf{x}')$$

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



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

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

$\zeta=k_f|x-x'|$

n: density of electron gas

Kohn-Sham

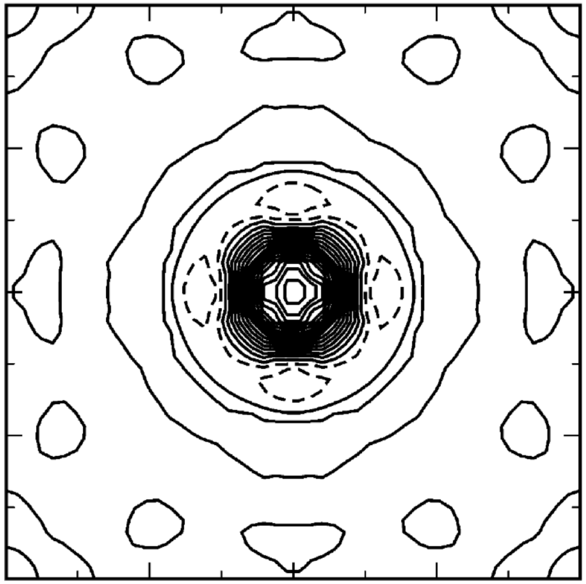


FIG. 4. Contour plot of the real-space density matrix for Al calculated in the {100} plane for the conventional cubic unit cell (the x-y axes are parallel to the bonds).

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)

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

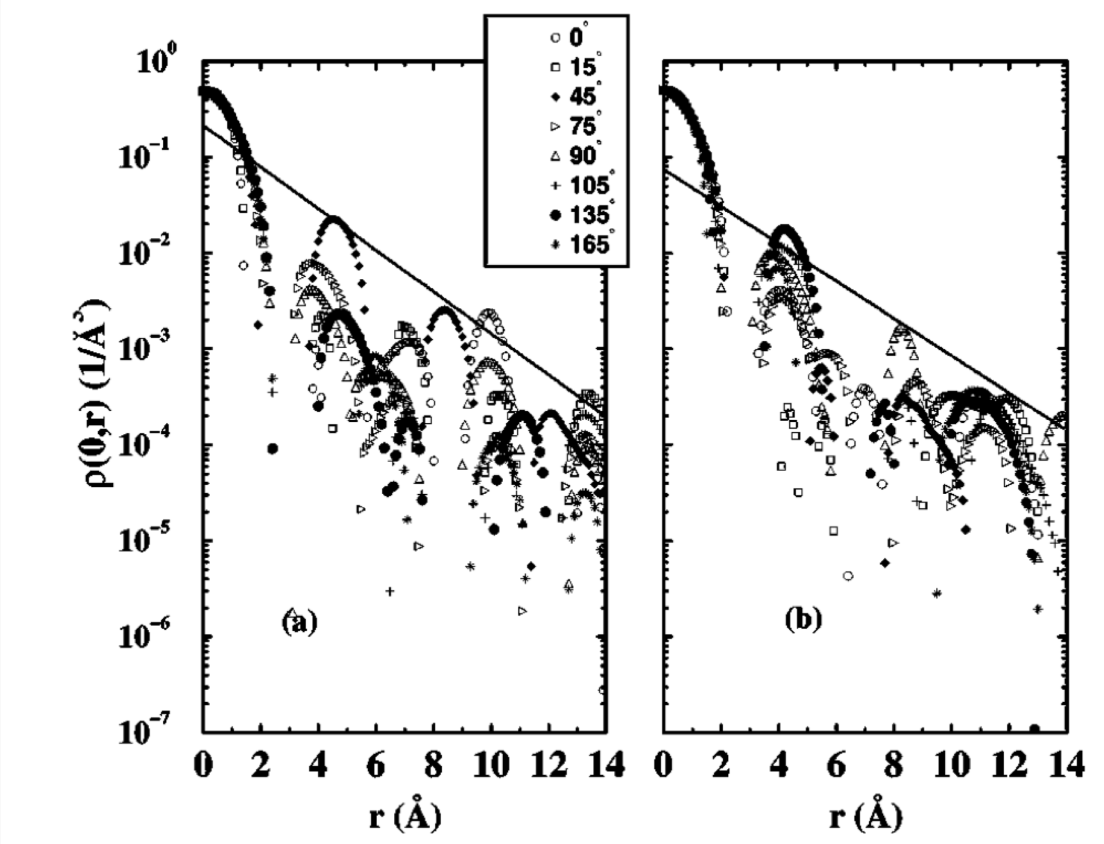
Σ is a (known) sum, depending on dimensionality D=1,2,3

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

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

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


Scanned at the American Institute of Physics

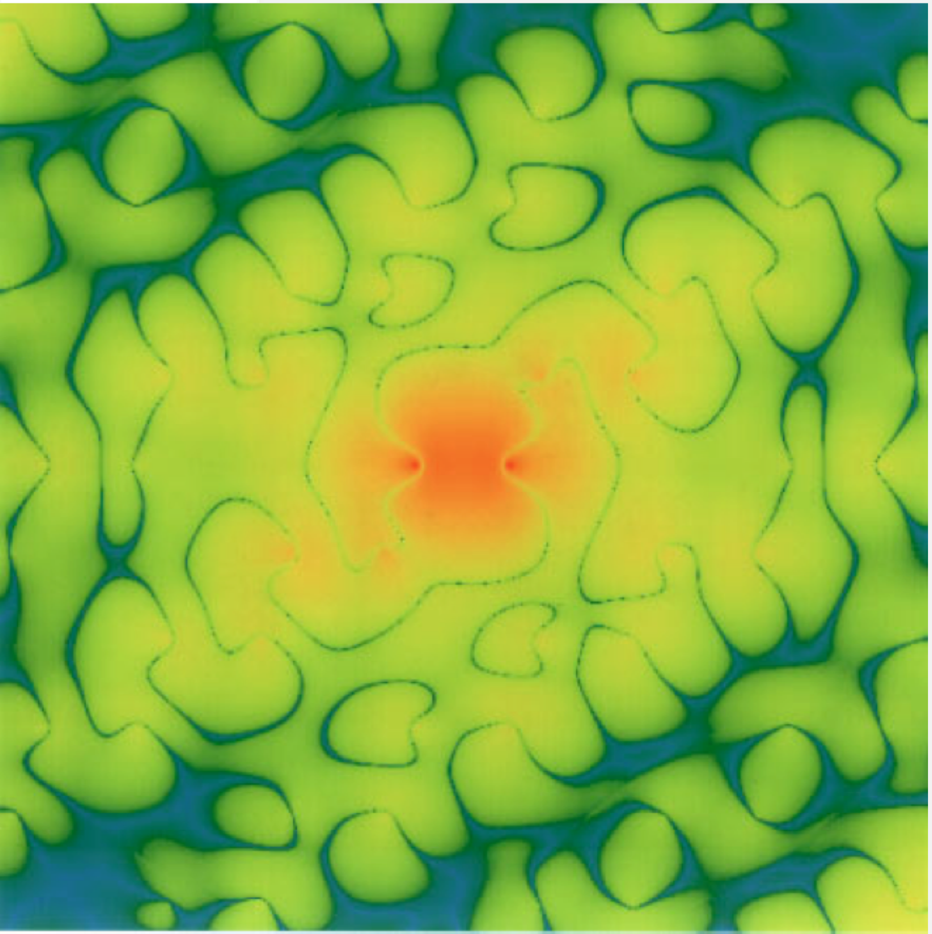
- Wannier functions: unitary transformations of eigenstates localized in real space.
- Not unique, *but* Vanderbilt showed how to compute maximally-localized Wannier functions[1].
- Long range decay of these is similar for c-Si and a-Si, and similar to decay of density matrix.
- We compute with an O(N)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

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

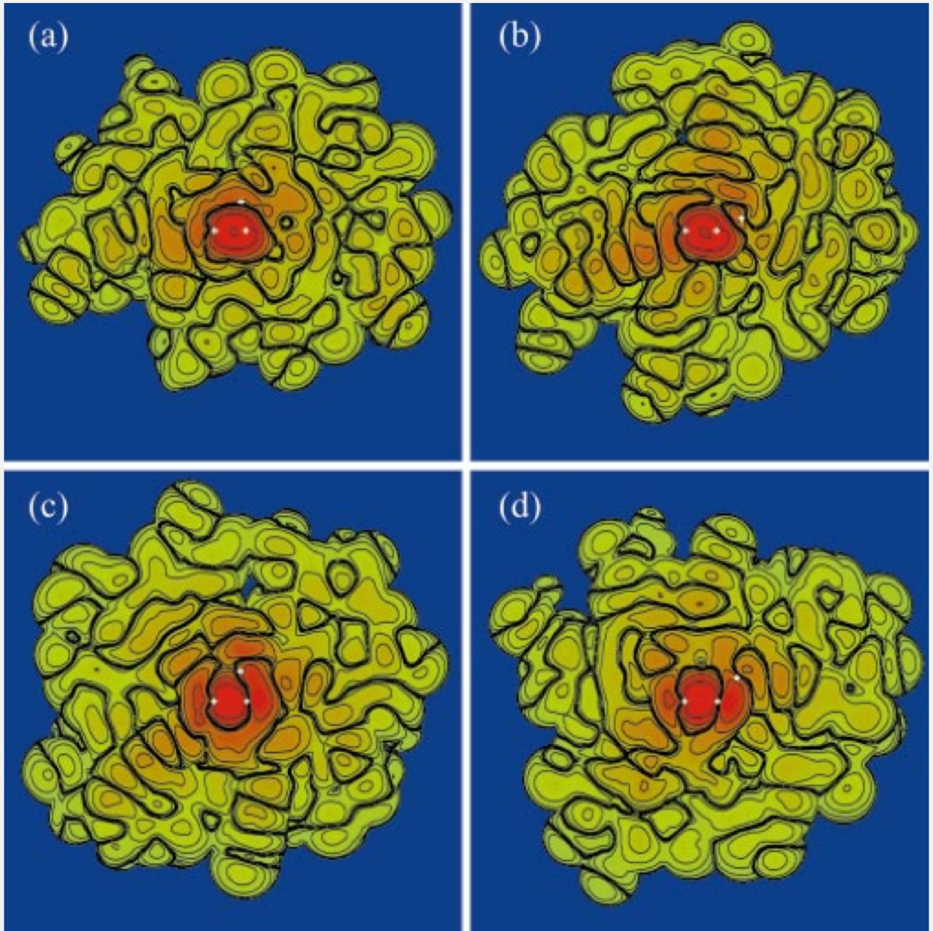
WANNIER FUNCTIONS FOR DISORDERED SYSTEMS

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

Diamond



a-Si



CONCLUSION: LOCALITY

We *quantify* Kohn's Principle:

(1) Analytically for two-band insulator

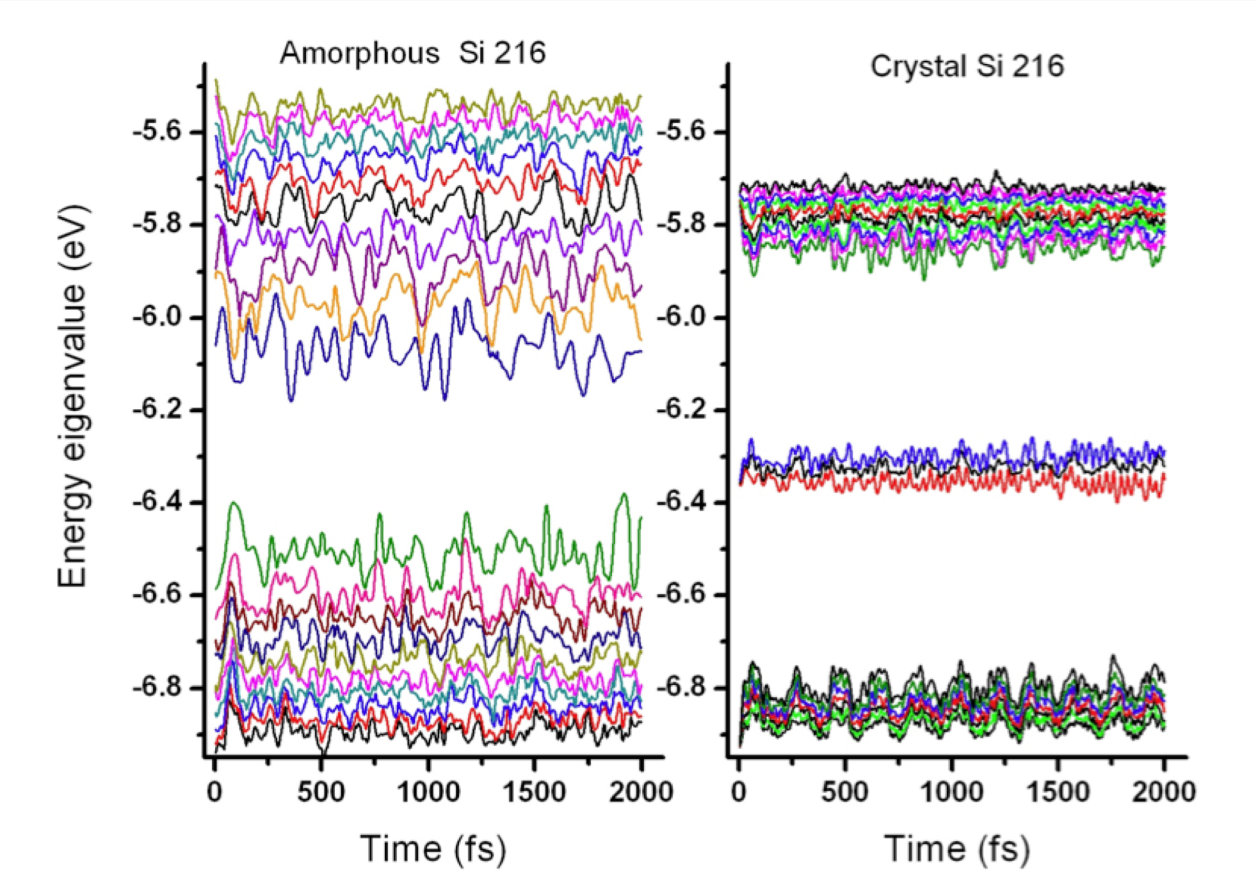
(2) By direct calculation of ρ with Kohn-Sham orbitals for metals, crystalline and amorphous semiconductors. Also Wannier functions from projection.

(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

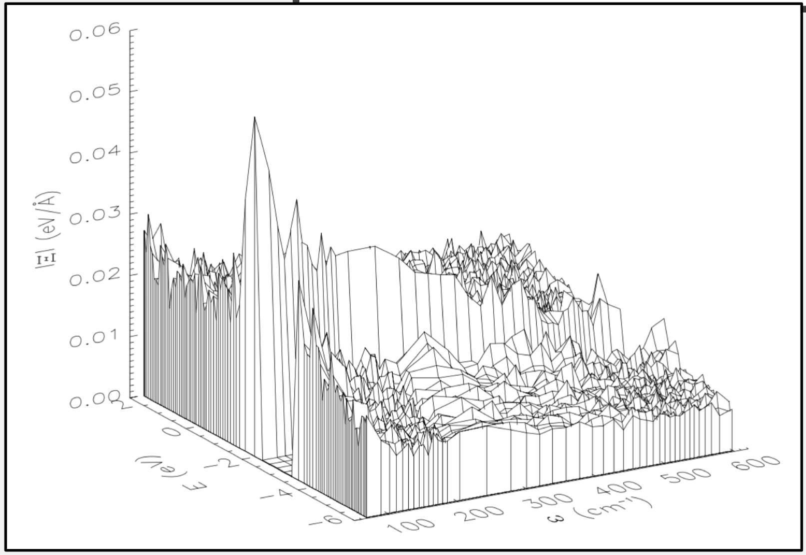
- Hellmann-Feynman theorem and harmonic approximation with classical lattice dynamics leads easily to fluctuations in electron energy eigenvalue $<\delta\lambda^2>$:

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

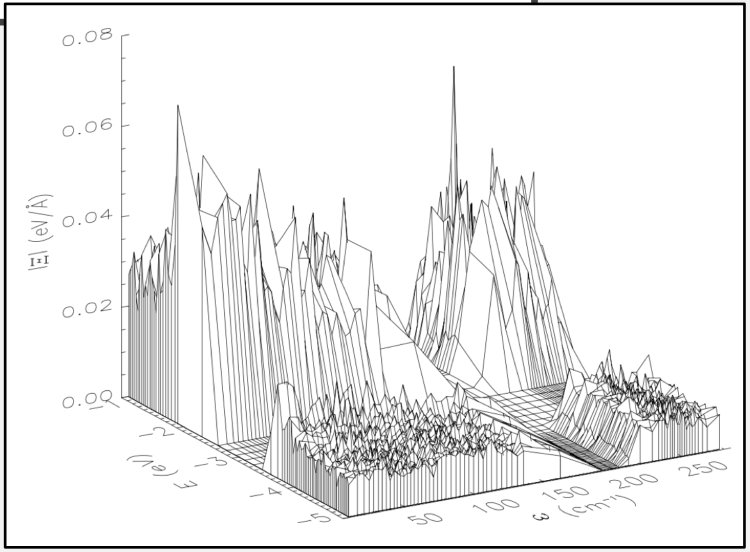
$$\Xi_n(\omega) = \sum_{\alpha=1}^{3N} \langle \psi_n | \frac{\partial \mathbf{H}}{\partial \mathbf{R}_\alpha} | \psi_n \rangle\, \chi_\alpha(\omega).$$

We call Ξ the electron-phonon coupling

E-P COUPLING: A-SI, A-SE



Si



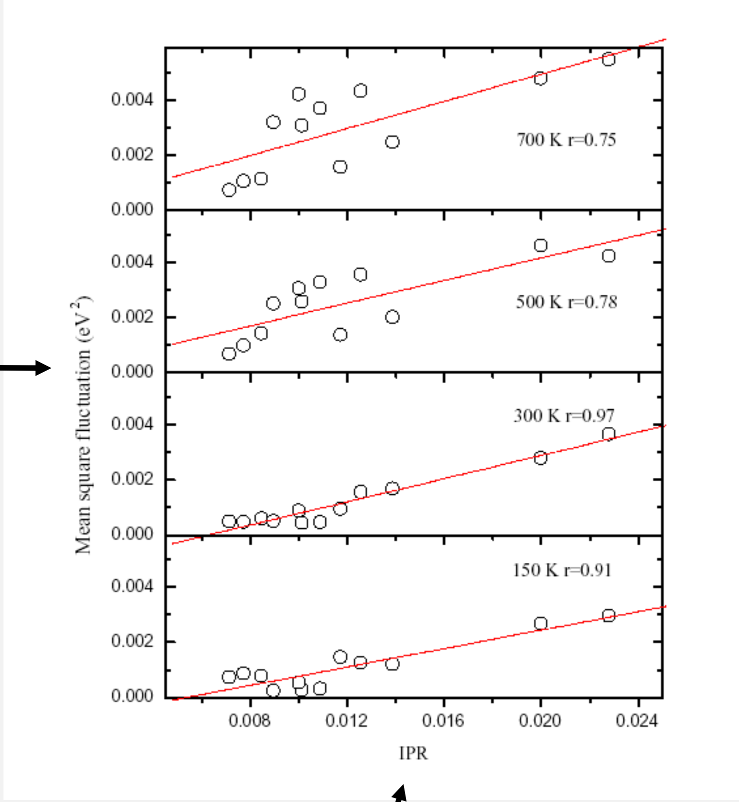
Se

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

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); K. Prasai *et al*., Sem. Sci. Tech. **31** 073002 (2016)

CORRELATION BETWEEN LOCALIZATION AND THERMAL FLUCTUATION FROM MD



700K

500K

300K

150K

$<\delta\lambda^2>$ →

(T>0 property)

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) $<\delta\lambda^2> \sim$ IPR

IPR = inverse participation ration; measure of localization

[1] K. Prasai, P. Biswas & DAD Sem. Sci. Tech. **31** 073002 (2016)

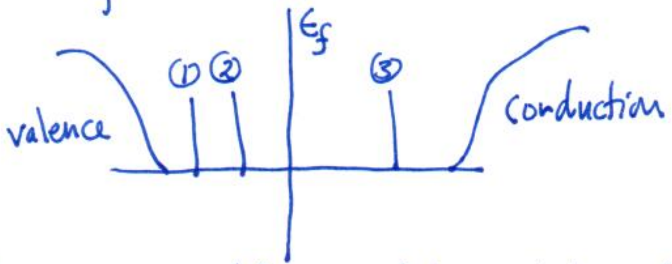
MATERIALS BY DESIGN
ENGINEERING THE GAP

Idea: We want a spectral region to include no electron states – we seek a model with a specified optical gap, or we want to impose a priori electronic information that an ideal model should have a particular gap…

Examples: band gap engineering for PV applications
: seeking conducting phases of semiconductors
: means to impose a priori optical info. in modeling

K. Prasai, P. Biswas and DAD, Sci. Rept. **5** 15522 (2015)
ibid., Phys Stat Sol A **213** 1653 (2016)

We have this density of electron states in our computer model:



① - ③ are unwanted gap states. Lets get rid of them! How?

Note: The total energy (in tight-binding) is:

$$\Phi = \underbrace{\sum_{n\,occ} \lambda_n}_{\text{Band energy}} + \underbrace{U}_{\text{Repulsive term}}$$

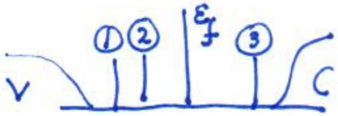
So the force is just

$$F_\alpha = -\frac{\partial \Phi}{\partial R_\alpha} = \sum_{n\,occ} -\frac{\partial \lambda_n}{\partial R_\alpha} - \frac{\partial U}{\partial R_\alpha}$$

R_α: atomic coordinate

$$F_\alpha = -\sum_{n\,occ} \frac{\partial \lambda_n}{\partial R_\alpha} - \frac{\partial U}{\partial R_\alpha}$$

Each term is a contribution to total force - eigenvalue by eigenvalue.



So any $\frac{\partial \lambda_n}{\partial R_\alpha}$ below ε_f provides a piece of the total force.

But... Consider $\partial\lambda_3/\partial R_\alpha$, the gradient of $\lambda_3(R_1 - R_{3n})$.

It indicates direction of maximum increase of λ_3.

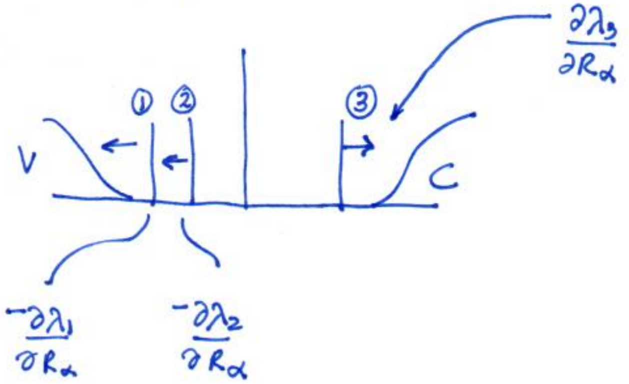
⇒ So to shift λ_3 toward conduction edge, move incrementally along $\underset{\sim}{e} = \partial\lambda_3/\partial R_\alpha$

Analogously, shift λ_1, λ_2 toward valence edge by moving along $-\partial\lambda_1/\partial R_\alpha$ etc (− for valence).

OK, so these $\partial\lambda_n/\partial R_\alpha$ gradients point the way to optimizing the gap. They are byproducts of any simulation thanks to the Hellmann-Feynman theorem

$$\frac{\partial\lambda_n}{\partial R_\alpha} = \langle\psi_n|\frac{\partial H}{\partial R_\alpha}|\psi_n\rangle \qquad H|\psi_n\rangle = \lambda_n|\psi_n\rangle \text{ etc}$$

Conceptually then, we add "gap-clearing forces" on states ①, ②, ③.



PRACTICAL IMPLEMENTATION

Consider a Lagrangian $\mathcal{L}$=T-Φ in which T is the usual kinetic energy, and

$$\Phi(R_1, R_2 \ldots, R_{3N}) = \sum_i f_i \langle \Psi_i | H | \Psi_i \rangle + U_r \longleftarrow \textit{usual forces}$$

$$\textit{“gap clearing” force} \longrightarrow + \sum_i{}' \gamma g(\lambda_n) \left(\langle \Psi_n | H | \Psi_n \rangle - \varepsilon_f \right)$$

g(λ_n) is picked to move valence (conduction) defect states into valence (conduction) tail.

Designed to push defect levels below E_f into the valence band, levels above E_f into conduction band.

GAP ENGINEERING: CONTINUED

Biased dynamics (with forces added to open gap) at diffusive temperatures leads to relaxed structures with engineered gap.

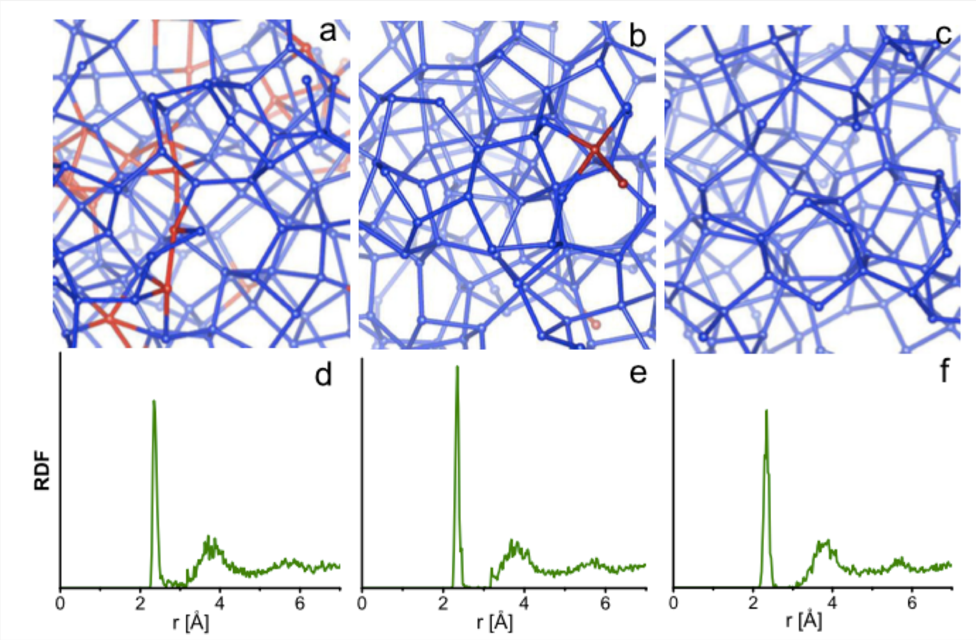
In practice we carry out the melt-quench segment of the simulation with biased forces. After dynamical arrest, we anneal and relax with physical forces and produce models with the desired optical gap.

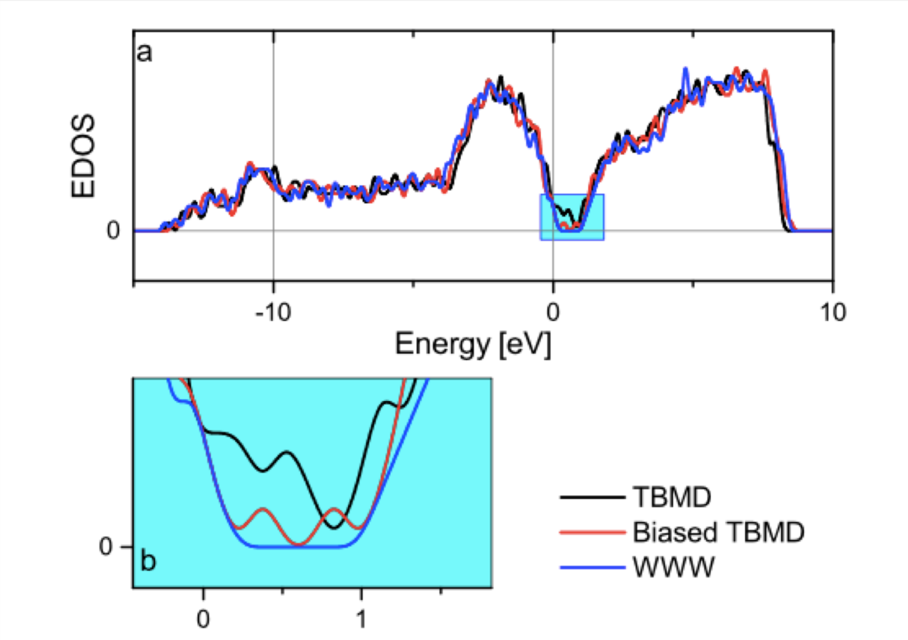
Implemented with ab initio code (VASP) and tight-binding.

EXAMPLE 1: CLEAN UP THE GAP IN A-SI

TBMD “gap force” WWW

Density of states

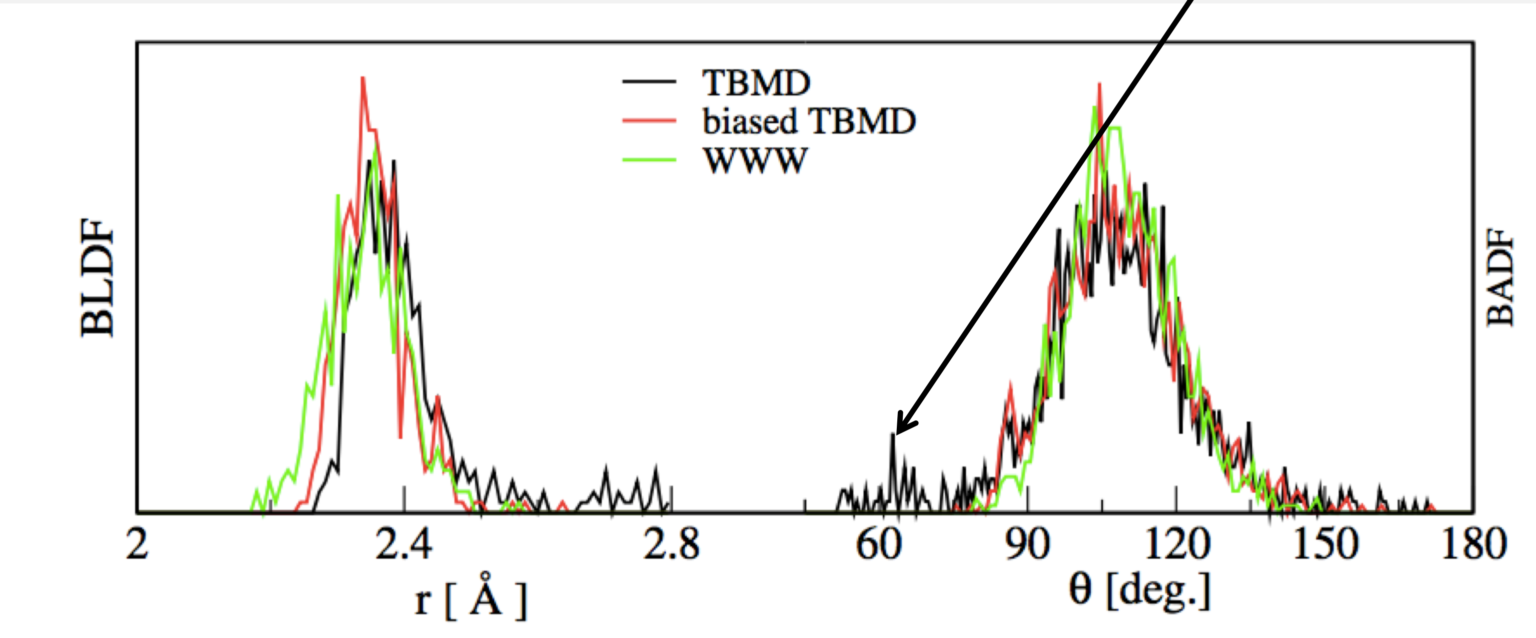




Red – coordination defects

97% fourfold (~87% tbmd)

RESULTS: A-SI



Defects: structural and electronic!

Note: STRUCTURAL features of "gap force" model is much better than TBMD, close to WWW. Electronic *a priori* information improves the structure.

Example II: close the gap in a-$(GeSe_3)_{1-x}Ag_x$ Materials

– Solid Electrolyte (incredibly mobile Ag in glassy host)

- Conducting bridge (FLASH) memory materials: insulating phase and conducting phase (real devices you can buy!)

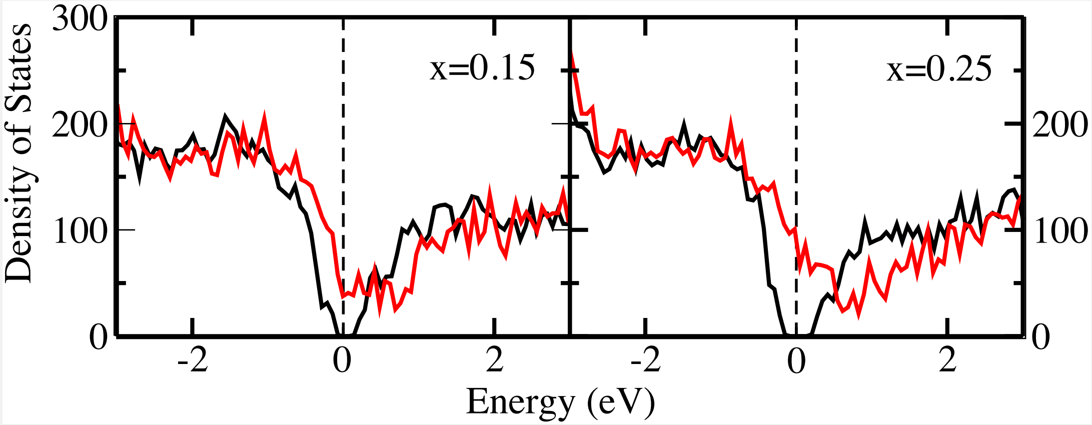
- Unclear identity of electronically conducting phase (little Ag wires or something else possible?)

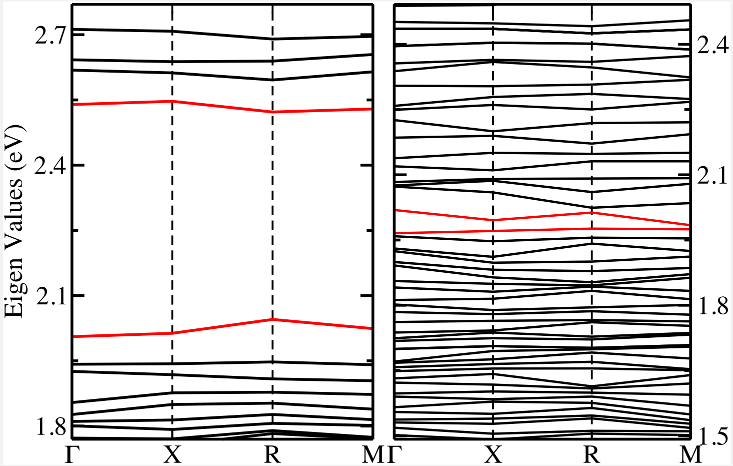
- Possible application for multilevel memory and neuromorphic computing applications.

- This Work: Determination of electronically conducting phase at $x=0.15$ and 0.25, about 0.04 eV/atom above best semiconducting glass models.

Electronic Structure: Metallic vs. Insulating

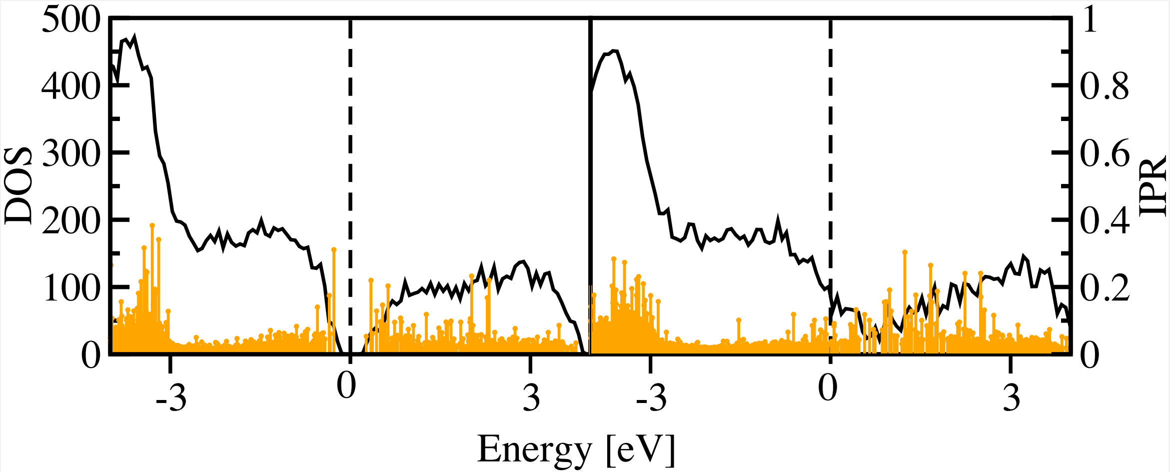
Black: Insulating, Red: Metallic





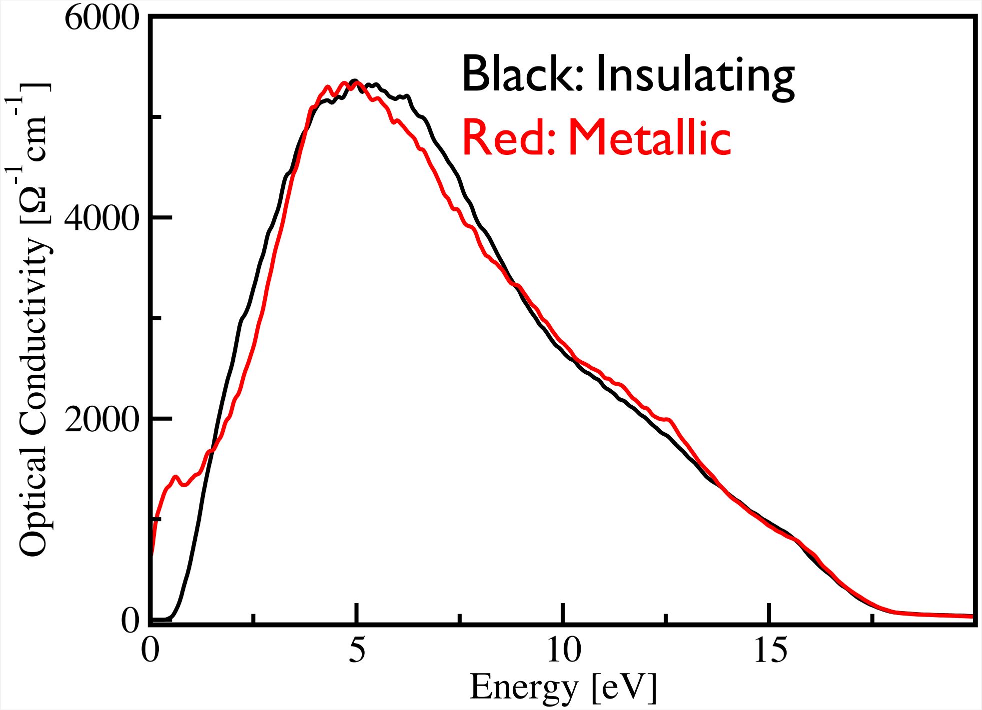
Red lines: HOMO-LUMO Levels

IPR: A measure of Localization



Optical Conductivity

Kubo-Greenwood Formula



DC Conductivity:

Insulating ~10^{-6} S/cm
Metallic ~10^{2} S/cm

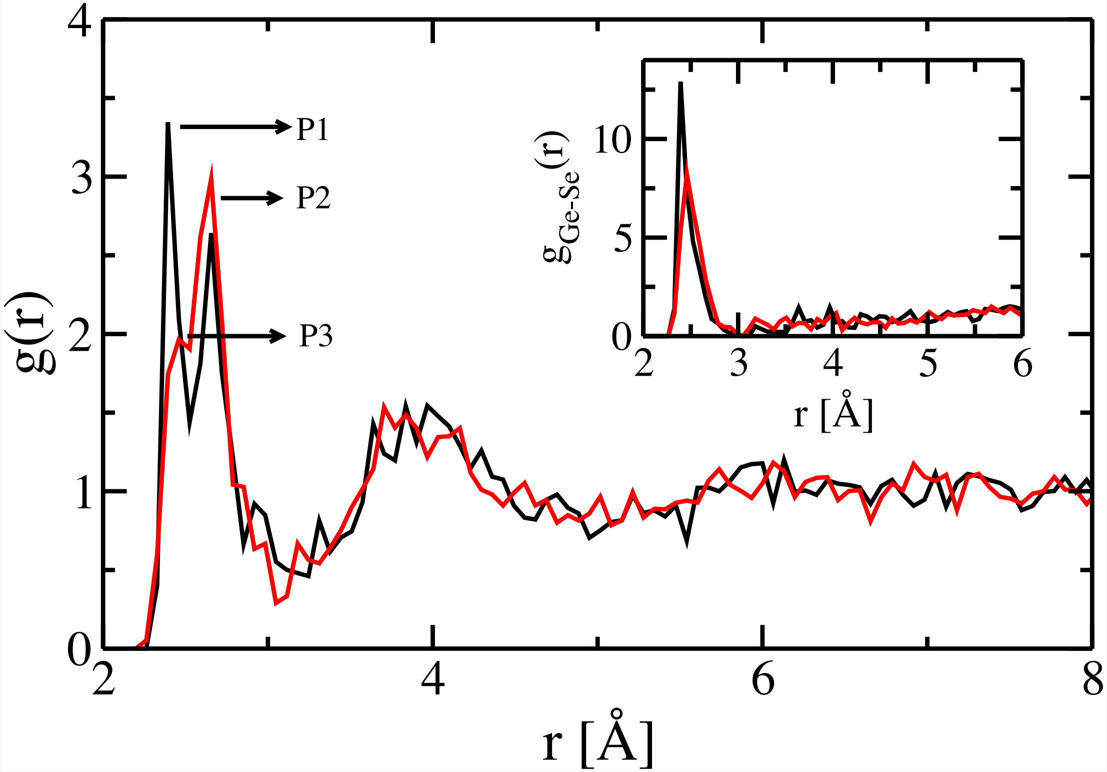
K. Prasai and DAD
Phys. Rev. Mater. **1** 015603 2017

Mechanism: impurity band hopping at Fermi-level, conduction Through Se p-orbitals ***not*** silver!

Pair Correlations

$(GeSe_3)_{1-x}Ag_x$: Ag_2Se and Ge_tSe_{1-t}

Black: Insulating, Red: Metallic



GAP ENGINEERING: CONCLUSION

- We give a practical recipe to impose a desired gap. (potentially useful for applications).

- Constraining the electronic structure has structural consequences. We offer means to include complex but important information in making a model that agrees with our full knowledge base

Can determine new phases of useful materials with desired electronic properties

ADDITIONAL TOPICS (AS TIME ALLOWS): REAL-SPACE PROJECTION OF THE ELECTRICAL CONDUCTIVITY AND NOVEL MODELING SCHEMES

ELECTRICAL CONDUCTIVITY

- Electronic conduction is key in applications.
- Emerging computer memory technology is all about conducting and insulating "paths" in materials.
- High Temperature Coefficient of Resistance (TCR) makes a-Si:H an ideal material for IR imaging (night vision) applications.
- We compute the conductivity using linear response theory: Kubo-Greenwood formula[1].


Scanned at the American Institute of Physics

R. Kubo, J. Phys. Soc. Jpn. **12** 570 (1957); D. A. Greenwood, Proc. Phys. Soc. **71** 585 (1958)

ESTIMATING THE CONDUCTIVITY

Thus, DC conductivity may be computed as the zero frequency limit. To include the motion of the lattice (thus temperature dependence), we average over the motion of the atoms from a simulation.

DC conductivity:

$$\sigma \propto \lim_{\omega \to 0} \frac{1}{\omega} \overline{\sum_{ik} (f_i - f_k) |<\psi_i | p | \psi_k>|^2 \delta(E_k - E_i - \hbar\omega)}$$

$\omega : frequency$

$\psi : wavefunction$

$E : energy\_eigenvalue$

$p : momentum\_operator$

$bar : thermal\_average$

We compute all this for credible structural models. Main T-dependence is in the thermal (trajectory) average!

CONDUCTING PATHS: DECONSTRUCTING THE KUBO GREENWOOD FORMULA

K. PRASAI, K. SUBEDI,

- **Kubo-Greenwood formula**: standard tool to compute electronic conductivity. From the atomistics (wave functions, energy eigenvalues) provides AC conductivity. Most physical derivation: Mott and Davis, first linear response theory (Kubo, Greenwood, Chester).
- The diagonal elements of conductivity tensor may be written in several equivalent ways, one. Is:

$$\begin{aligned}\sigma_{\alpha\alpha}(\omega) &= \frac{2\pi e^2\hbar}{\Omega m^2}\sum_{ni}|\langle\psi_n|p_\alpha|\psi_i\rangle|^2\frac{f_F(\varepsilon_i)-f_F(\varepsilon_n)}{\hbar\omega}\\ &\times\ \delta(\varepsilon_n-\varepsilon_i-\hbar\omega) \qquad (1\end{aligned}$$

K. Prasai, P. Biswas, K. Subedi, K, Ferris and D.A. Drabold, Spatial projection of electronic conductivity, the example of conducting bridge computer memory, PSS Rapid Research Letters, https://doi.org/10.1002/pssr.201800238

EXTRACTING REAL-SPACE INFORMATION ABOUT CONDUCTIVITY

- Usually we make a model, want to know (say) DC conductivity. So compute Kohn-Sham eigenvalues and vectors, momentum matrix element and hey presto, R=7.2 kΩ. *Can we extract more information?*
- Here, I show how to get a Space Projected Conductivity (SPC) – what parts of the cell are active in conduction, which are not?
- Strategy is simple: write out Kubo-Greenwood formula as a sum involving Kohn-Sham orbitals in real space, leaving an expression of the form: conductivity $= \Sigma_x$ [SPC(x)] $= \Sigma_x \zeta(x)$ – *find the SPC function that achieves this*
- *For $\omega > 0$, tells us which parts of the network absorb energy for external radiation field (light!) at that frequency.*

$$\sigma_{\mathbf{k}}(\omega) = \sum_{i,j} g_{ij}(\mathbf{k},\omega) \sum_{\alpha} |p_{ij}^{\alpha}|^2. \tag{1}$$

So by direct substitution:

$$\sigma = \sum_{ij\alpha} \int d^3x \int d^3x' \, g_{ij} \, [\psi_j^*(\mathbf{x}) p^{\alpha} \psi_i(\mathbf{x})][\psi_i^*(\mathbf{x}') p^{\alpha} \psi_j(\mathbf{x}')] \tag{2}$$

OK, so now imagine a real-space grid, call the points {x} – we can discretize the integrals as a double sum (on x,x'), compute the operation of p from finite differences. Then define complex-valued functions on the grid points:

$$\xi_{ij}^{\alpha}(\mathbf{x}) = \psi_i^*(\mathbf{x}) p^{\alpha} \psi_j(\mathbf{x})$$

Then we have expressed the conductivity as a discrete spatial double sum (suppose uniform grid spacing in 3D, call it h), so….

$$\sigma \approx h^6 \sum_{\mathbf{x},\mathbf{x}'} \sum_{ij\alpha} g_{ij} \xi^{\alpha}_{ji}(\mathbf{x}) \xi^{\alpha}_{ij}(\mathbf{x}').$$

Define the Hermitian, positive semidefinite matrix

$$\Gamma(\mathbf{x},\mathbf{x}') = h^6 \sum_{ij\alpha} g_{ij} \xi^{\alpha}_{ji}(\mathbf{x}) \xi^{\alpha}_{ij}(\mathbf{x}'), \qquad (4)$$

Then:

$$\sigma = \sum_{\mathbf{x}} \Gamma(\mathbf{x},\mathbf{x}) + \sum_{\mathbf{x},\mathbf{x}',\mathbf{x}\neq\mathbf{x}'} \Gamma(\mathbf{x},\mathbf{x}') \qquad (5)$$

SPATIALLY PROJECTED CONDUCTIVITY (SPC)

Take: SPC $= \zeta(x)=|\Sigma_\alpha \Gamma(x,\alpha)|$. In practice, the positive, diagonal approximation $\zeta(x)=\Gamma(x,x)$ is qualitatively similar.

In this case we then have: $\sigma(\omega)=\Sigma_x \Gamma(x,x)=\mathrm{Tr}(\Gamma)$.

SPECTRAL DECOMPOSITION: Γ IS HERMITIAN, SO DIAGONALIZE IT.

$$\Gamma|\chi_\mu\rangle = \Lambda_\mu|\chi_\mu\rangle$$

Λ has units of conductivity, so diagonalize Γ and:

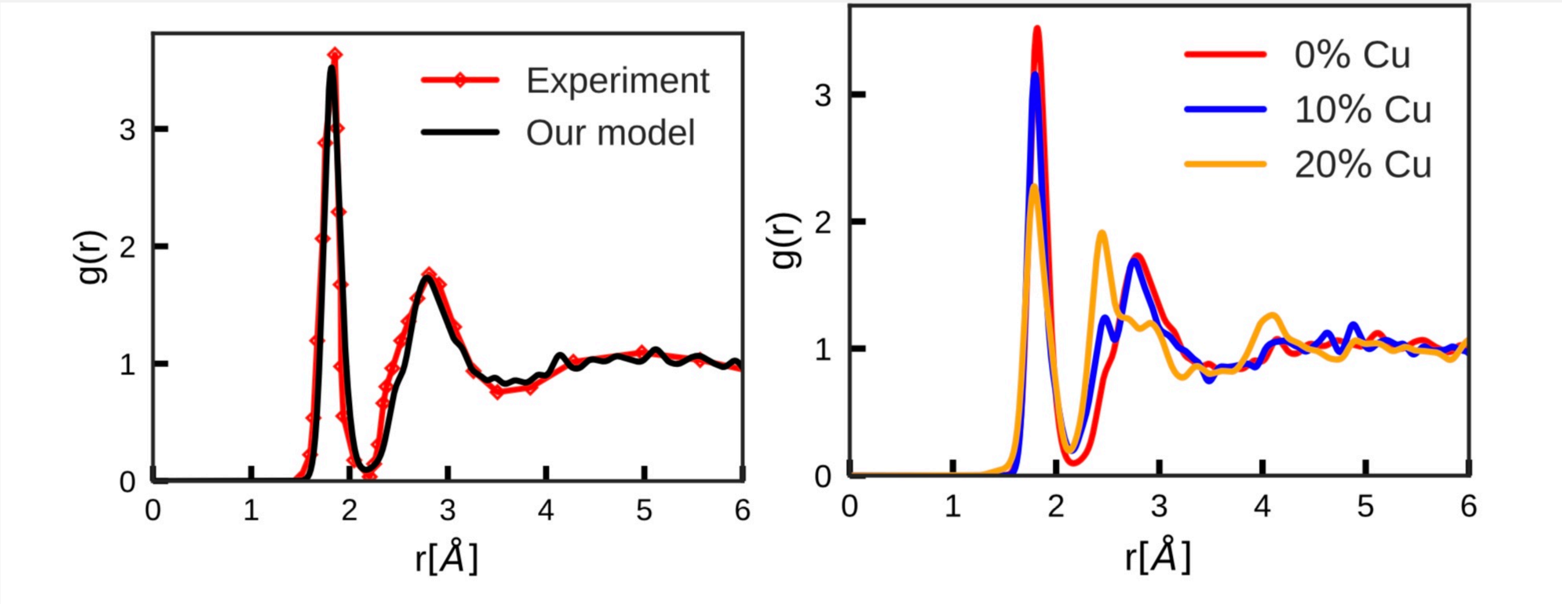
$$\sigma = \sum_{\mathbf{x}}\sum_{\mu}\Lambda_\mu|\chi_\mu(\mathbf{x})|^2 + \sum_{\mathbf{x},\mathbf{x}',\mathbf{x}\neq\mathbf{x}'}\sum_{\mu}\Lambda_\mu\chi_\mu(\mathbf{x})\chi^*_\mu(\mathbf{x}'), \tag{6}$$

We have *"eigenmodes of conductivity"*

TRY IT OUT:

- We've tried this on FCC Aluminum, diamond Si, doped a-Si etc.
- We reproduce the usual KG results from VASP, and recent paper of Trickey *et al.*
- Details: typically ~45x45x45 points is enough: dim(G)=91000]

CBRAM 1: AL_2O_3+CU MODELS (~200 ATOMS, VASP)



Left: alumina: model and experiment[1] Right: g(r) for 0, 10%, 20% Cu

---

[1] P. Lamparter, R. Kneip, Physica B 234-6 405 (1997).

CBRAM II: **CU CLUSTERS** IN AL_2O_3

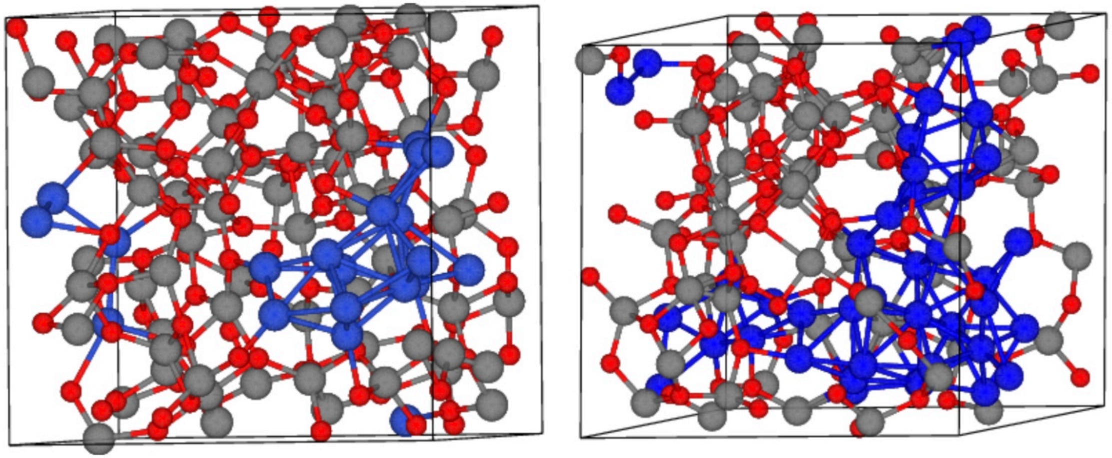


FIG. 2. Cu atoms (blue), O (red) and Al (grey) in $(a\text{-}Al_2O_3)_{.9}Cu_{.1}$ (top) and $(a\text{-}Al_2O_3)_{.8}Cu_{.2}$ (bottom). Note that the Cu clusters in the oxide matrix. Periodic boundary conditions are employed throughout.

Note 1: space-filling Cu cluster for 20% Broken link in 10%.

Note 2: clustering in Alumina, not in chalcs.

PROPERTIES OF Γ

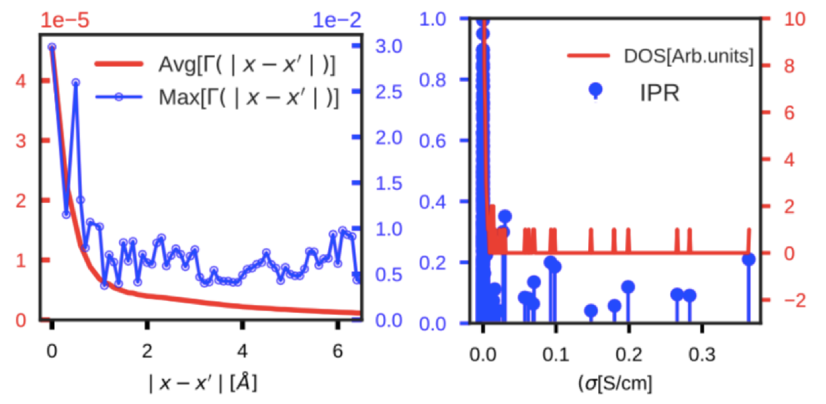
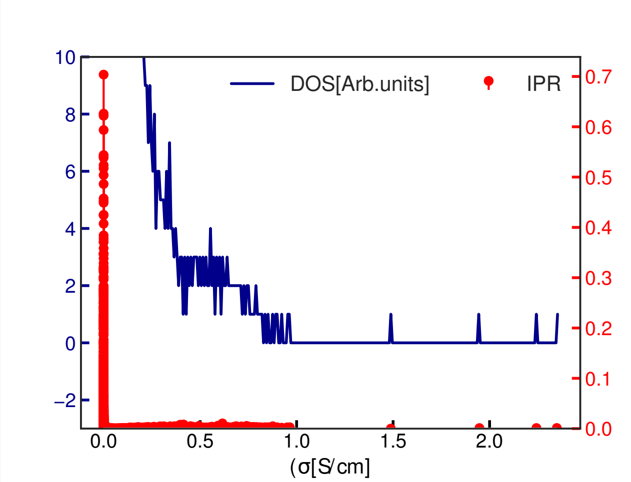


FIG. 3. Properties of $\Gamma(\mathbf{x}, \mathbf{x})$ for 10% Cu-doped model. Left: Decay of Γ matrix; Right: Spectrum of Γ and localization[23] of its eigenvectors (χ)

10% Cu-doped ALUMINA
Left: Γ decay, right spectral properties of Γ



ALUMINUM
Note: only a few Λ are nonzero out of ~100,000. All the "big" Λ vectors are very extended, others very localized. *Note the "tail" for metallic system.*

Γ PROPERTIES: CONTINUED

- $\Gamma(x,y)$ falls off nicely as function of $|x-y|$. Much like Kohn's *Principle of Nearsightedness*.
- If one adopts the "diagonal approximation" SPC=$\zeta(x)=\Gamma(x,x)$ and compare attempts to include some off-diagonal information the details vary, the qualitative pictures do not.
- The spectral properties of Γ are very interesting, just starting to understand them.

BADER PROJECTION ONTO ATOMIC SITES

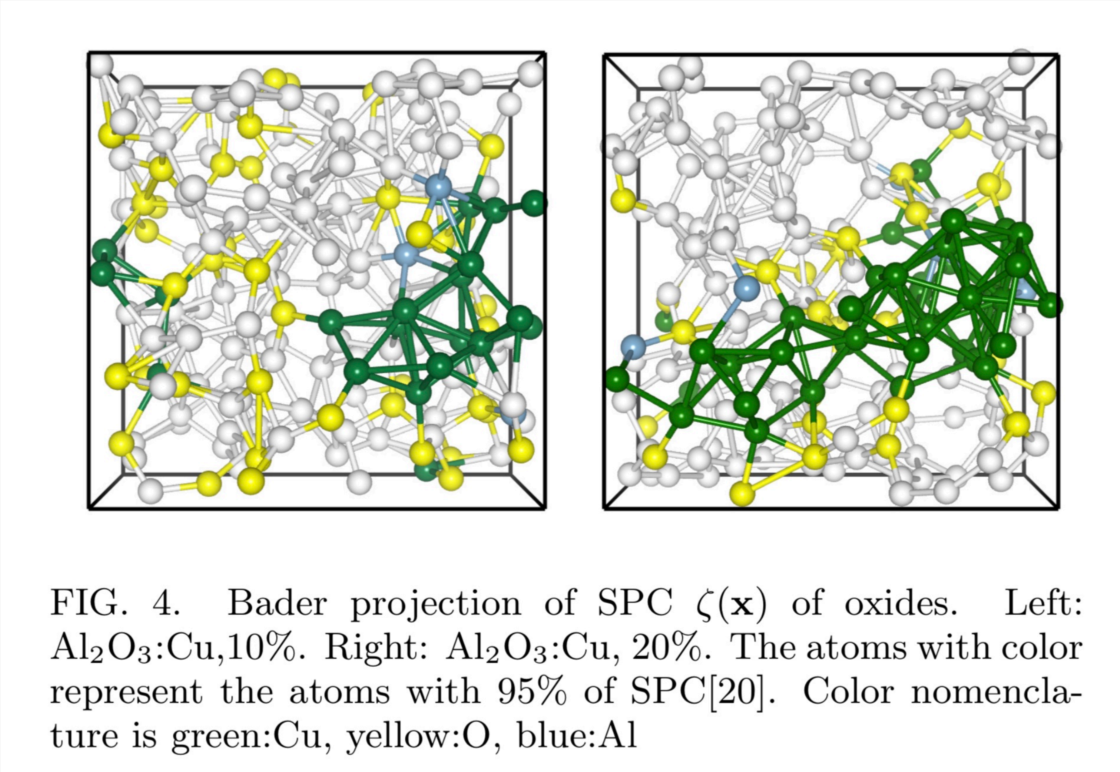


FIG. 4. Bader projection of SPC $\zeta(\mathbf{x})$ of oxides. Left: Al_2O_3:Cu,10%. Right: Al_2O_3:Cu, 20%. The atoms with color represent the atoms with 95% of SPC[20]. Color nomenclature is green:Cu, yellow:O, blue:Al

SPECTRAL REPRESENTATION: ISOSURFACES FROM 20 EVECS OF Γ (LEFT), ALL (RIGHT)

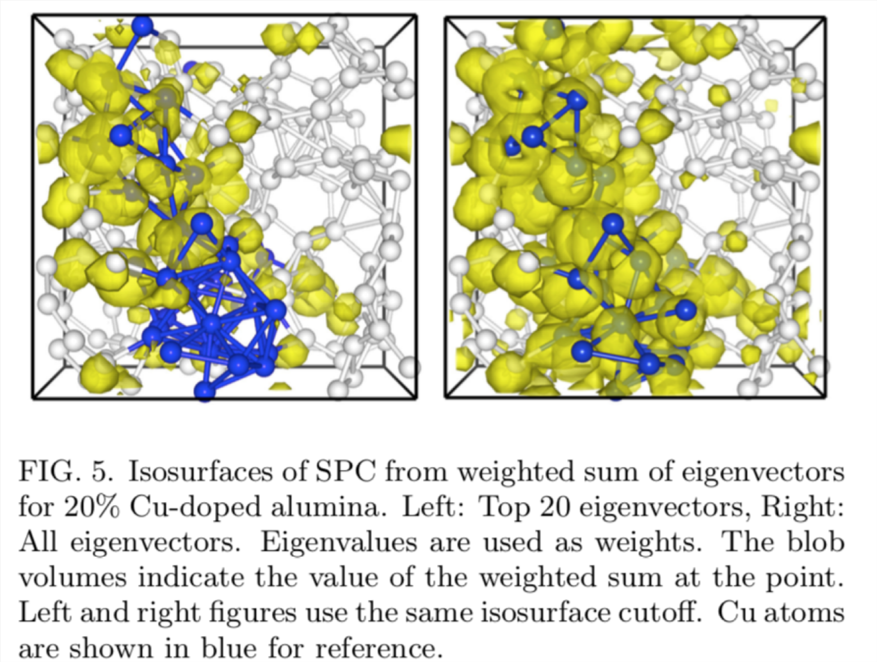


FIG. 5. Isosurfaces of SPC from weighted sum of eigenvectors for 20% Cu-doped alumina. Left: Top 20 eigenvectors, Right: All eigenvectors. Eigenvalues are used as weights. The blob volumes indicate the value of the weighted sum at the point. Left and right figures use the same isosurface cutoff. Cu atoms are shown in blue for reference.

Very similar to $\zeta(x)$, but decomposed into "conduction modes"

GREY SCALE MAPPING OF SPC

TOP: SEMICONDUCTING
GESE$_3$AG
MIDDLE: 10% CU
BOTTOM, 20% CU

K. Prasai, P. Biswas, K. Subedi, K, Ferris and D.A. Drabold, PSS Rapid Research Letters, https://doi.org/10.1002/pssr.201800238

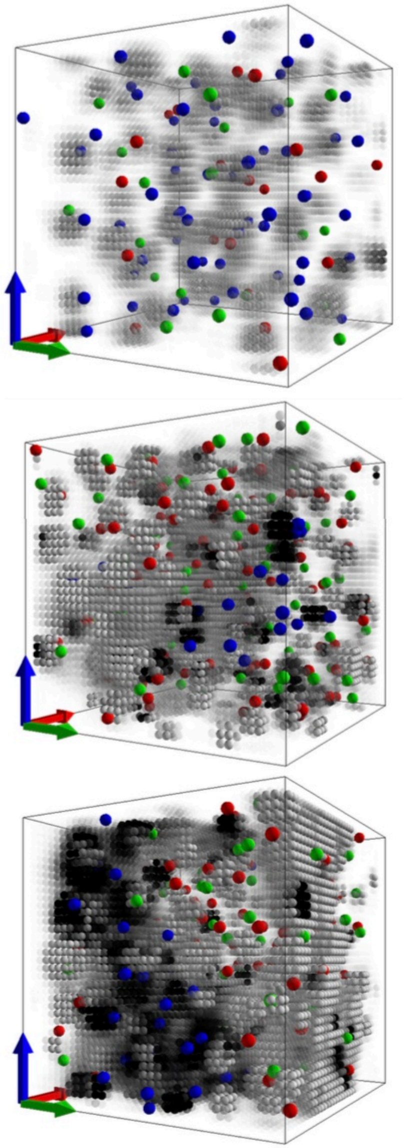


FIG. 6. Space-projected conductivity $\zeta(\mathbf{x})$ for a-$(\mathrm{GeSe}_3)_{.75}\mathrm{Ag}_{.25}$ (top) (a-$\mathrm{Al}_2\mathrm{O}_3)_{.9}\mathrm{Cu}_{.1}$ (middle) and (a-$\mathrm{Al}_2\mathrm{O}_3)_{.8}\mathrm{Cu}_{.2}$ (bottom). O and Ge atoms are shown in red, Cu and Se atoms in blue, and Al and Ag atoms in green. The SPC at each grid point is shown in grayscale which is scaled by either the mean ($\mathrm{Al}-2\mathrm{O}_3$:Cu) or the maximum (a-$(\mathrm{GeSe}_3)_{.75}\mathrm{Ag}_{.25}$) value of $\zeta(\mathbf{x})$.

CONCLUSIONS ON CONDUCTIVITY

- This seems to actually work. If you look at electronic DOS near E_f, delocalized states banding through Cu are notable at 20%, more localized and with some spectral gap for 10% Cu, and for GeSeAg, Ag is completely uninvolved in gap/tail states, its all Se 3p.
- Lots of interesting things to try like phase-change memory materials.
- Interesting "basic physics" asymptotics of Γ, new dynamical effects (electron-phonon coupling etc)
- Could we adapt the same idea to the KGF for thermal transport?
- The dimensionality of the grid is a problem if we diagonalize, and even then the problem is ideal for Lanczos.

MODELING PARADIGMS AND IMPOSING *A PRIORI* INFORMATION

1) **Simulation**: Implement your best calculation (big cell, fancy interactions, long time evolution, *etc*). *Hope* that the results look like experimental ones.
2) **Information:** Try to invert the experimental data.
3) **Merge the two**: carry out simulation but impose the *a priori* (possibly experimental) information as part of the simulation.

INFORMATION PARADIGM: REVERSE MONTE CARLO

KAPLOW, MCGREEVY *ET AL.*

- **Information paradigm**. *What does experiment imply about the structure?*
- "Reverse Monte Carlo" : put atoms in a supercell, move at random with Monte Carlo, keep moves if closer to experiment, accept with Metropolis probability if worse.
- Result: matches experiment by construction, but diffraction data **alone** is **insufficient** to produce a chemically realistic model. *Still, it is a clever idea -- **use the information you have**!*

RMC: DISCUSSION

- Promising ***if*** additional information (constraints) are employed. Has *sort of* worked for a-Si (but still only 88% fourfold).
- Has special flexibility to build in *a priori* information.
- Constraints are dangerous: we are imposing information, but we are potentially imposing errors – *the model is only as good as the information employed*!

FORCE ENHANCED ATOMIC REFINEMENT (FEAR): TEACH RMC CHEMISTRY

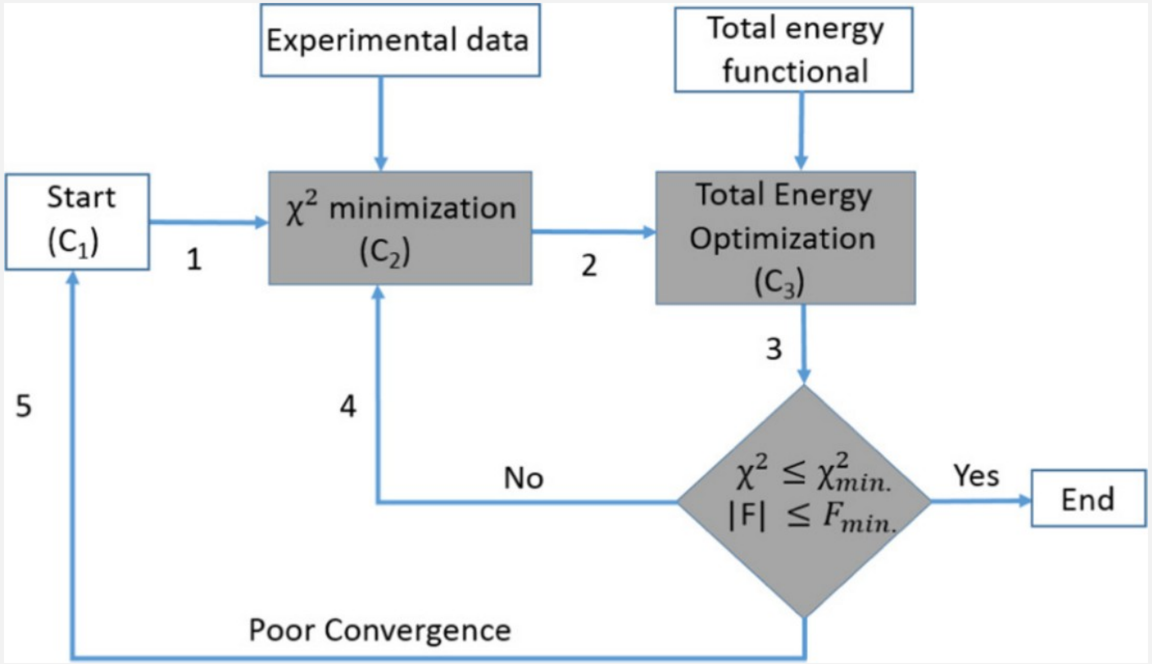
- Start with random model (assume density is known)
- Repeat to these two steps convergence:

-- Obtain N accepted moves from RMC [drives model toward experiment]

-- Take M conjugate gradients steps with energy functional [enforce chemistry]

Typically N~100, M~1-5. Always N>>M.

FORCE ENHANCE ATOMIC REFINEMENT (FEAR)



Partial Structural minimization

Partial Energy minimization

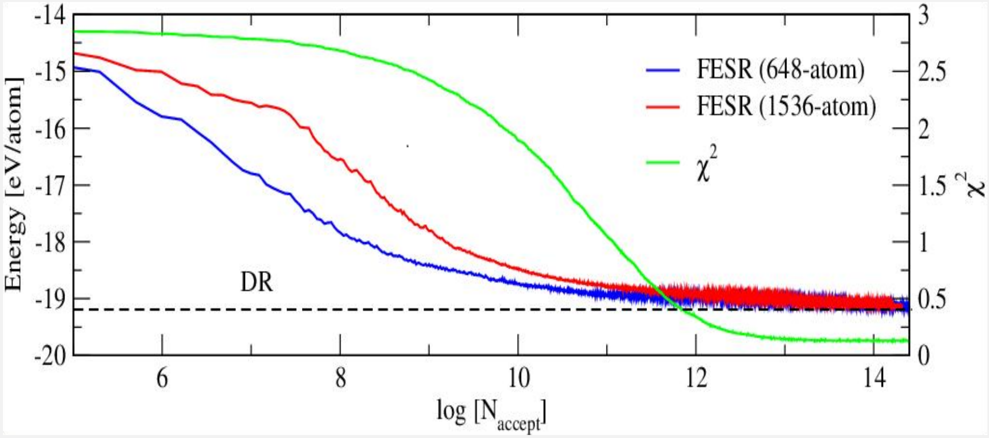
Pandey et. al, Phys.RevB 94, 235208 (2016)

EXAMPLE: FEAR FOR AMORPHOUS SIO_2

- Adopt 648-atom, 1536-atom models.
- Use the van Beest (BKS) potential (PRL, 1990). Start with **random** coordinates.
- After 100 successful RMC moves, move all the atoms along van Beest gradient – only one step, *not a full minimization.*
- *Repeat previous until convergence (fit and force) is achieved.*
- Need about 30,000 force calls

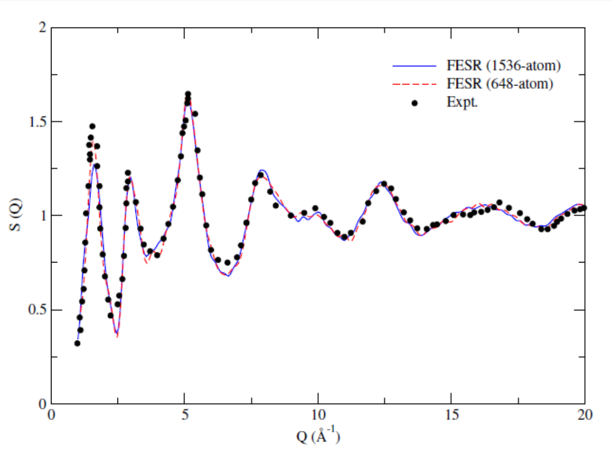
A. Pandey, P. Biswas, DAD Phys Rev B 92 155205 (2015)

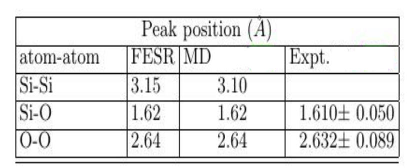
FEAR OF SILICA



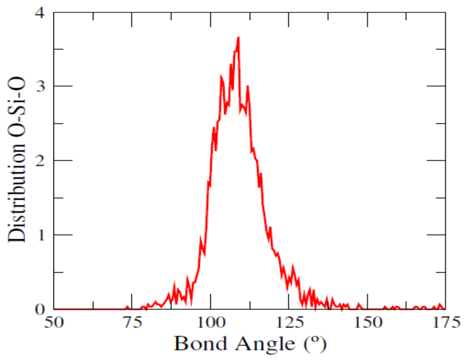
FEAR: minimization of error vs. experiment and total energy.

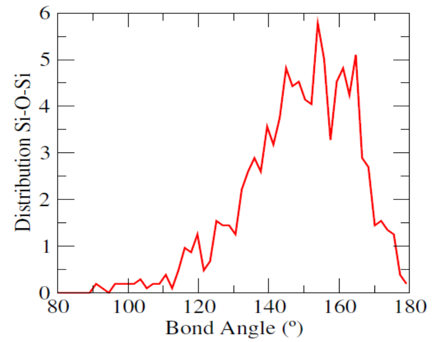
RESULTS: SILICA

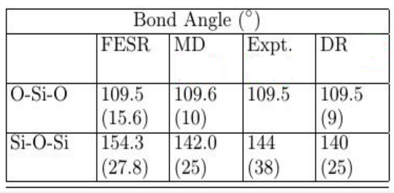




Peak position (Å)			
atom-atom	FESR	MD	Expt.
Si-Si	3.15	3.10	
Si-O	1.62	1.62	1.610± 0.050
O-O	2.64	2.64	2.632± 0.089





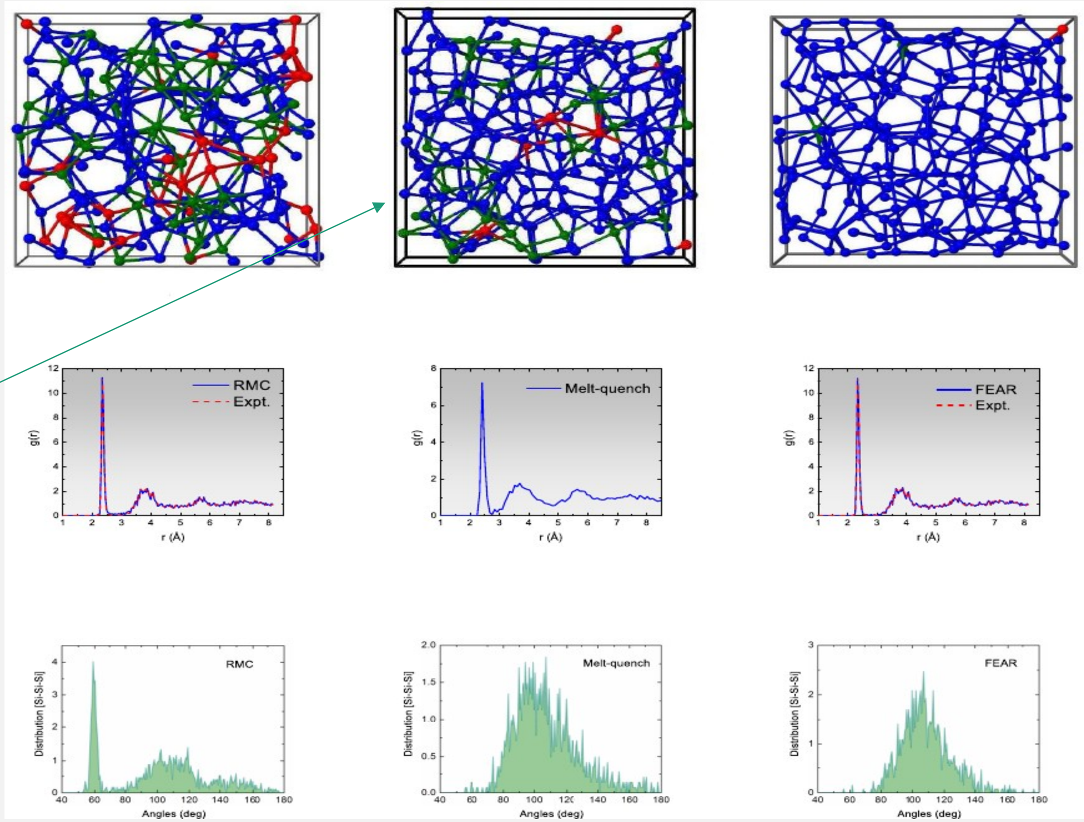


Bond Angle (°)				
	FESR	MD	Expt.	DR
O-Si-O	109.5 (15.6)	109.6 (10)	109.5	109.5 (9)
Si-O-Si	154.3 (27.8)	142.0 (25)	144 (38)	140 (25)

AB INITIO FEAR – USE DFT (VASP OR SIESTA) AS ENERGY FUNCTIONAL

- First example: silicon and SIESTA

RMC MELT QUENCH FEAR



RMC

Melt-Quench

FEAR

Blue: 4-fold

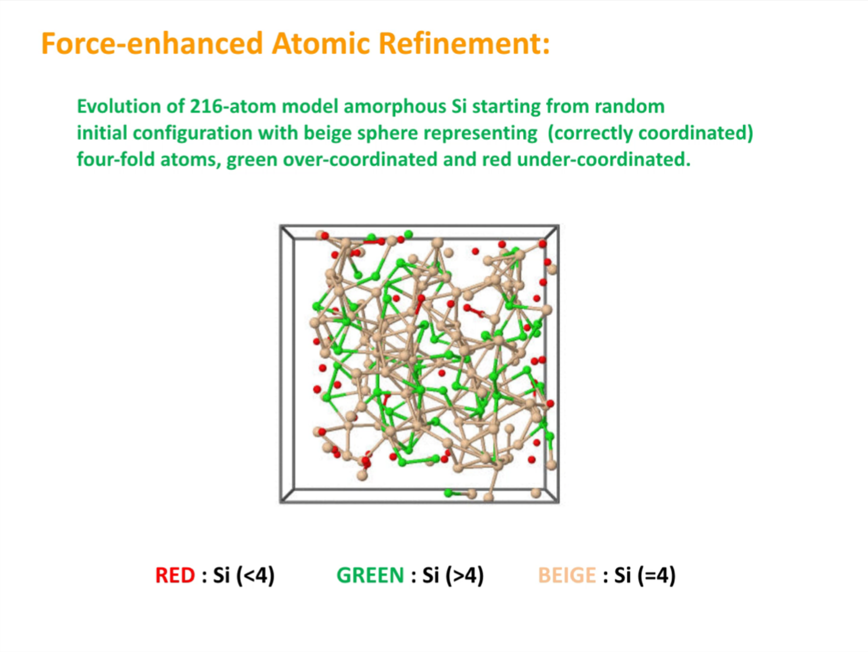
Green, Red

are

coordination defects

Pandey et. al, Scientific reports 6, 33731(2016), JNCS J. Non-Cryst. Sol 492 27 (2018).

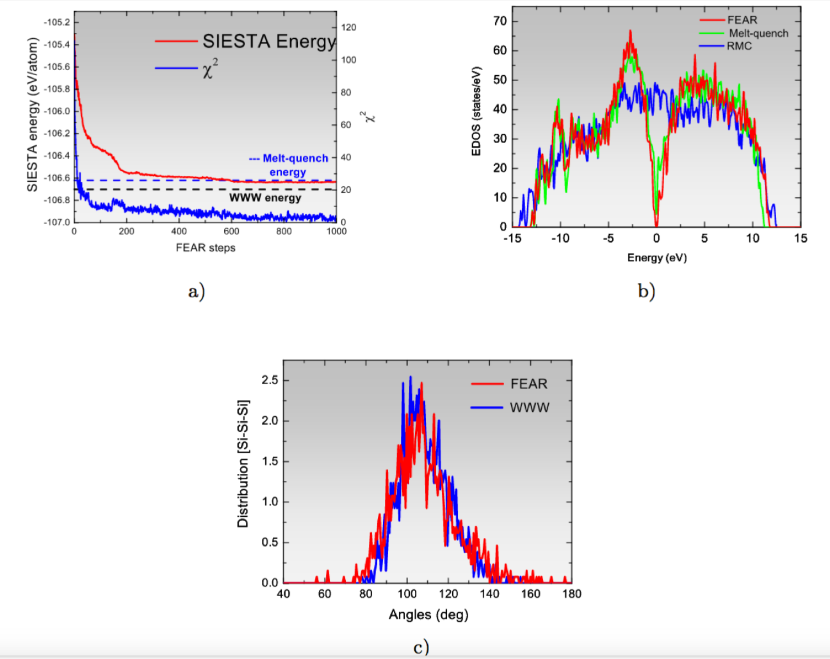
FEAR: A-SI ANIMATION AND DETAILS



Force-enhanced Atomic Refinement:

Evolution of 216-atom model amorphous Si starting from random initial configuration with beige sphere representing (correctly coordinated) four-fold atoms, green over-coordinated and red under-coordinated.

RED : Si (<4) **GREEN** : Si (>4) **BEIGE** : Si (=4)



a)

b)

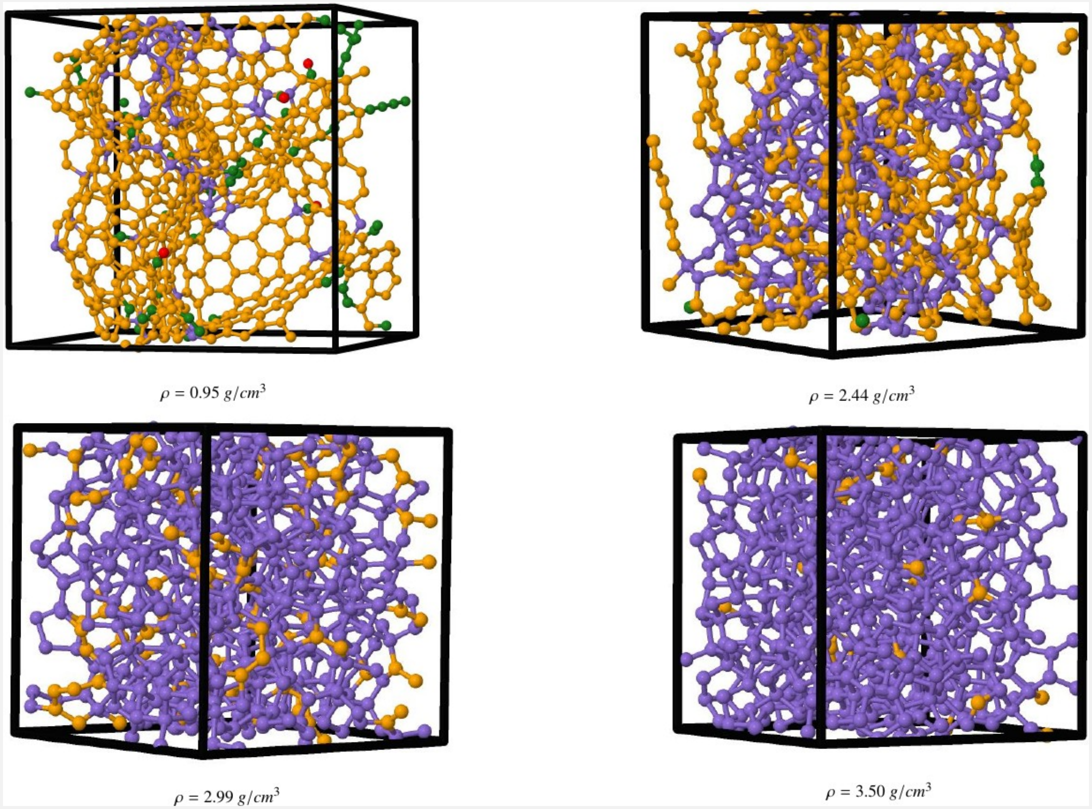
c)

EXAMPLE: LETS TRY AMORPHOUS CARBON ACROSS DENSITIES

- Hard: Carbon happily sp^3, sp^2 or even sp bonds. Need a good potential.
- Wealth of experiments to check against.
- We carry this out with largish models (up to 800 atoms), SIESTA as energy functional. Then relax final models with VASP (little change).

AMORPHOUS CARBON ACROSS DENSITIES

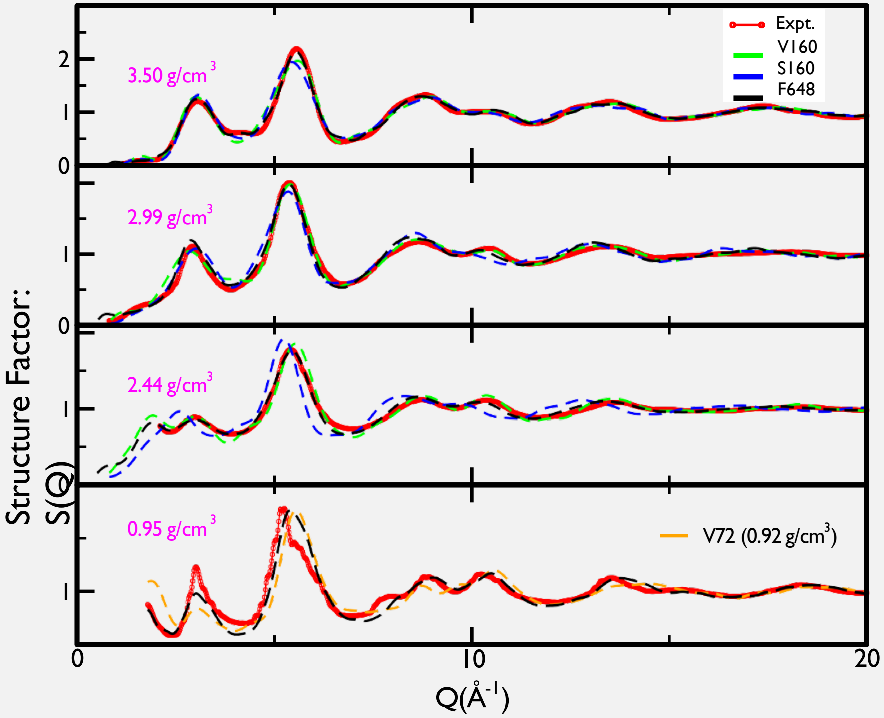
648 atoms

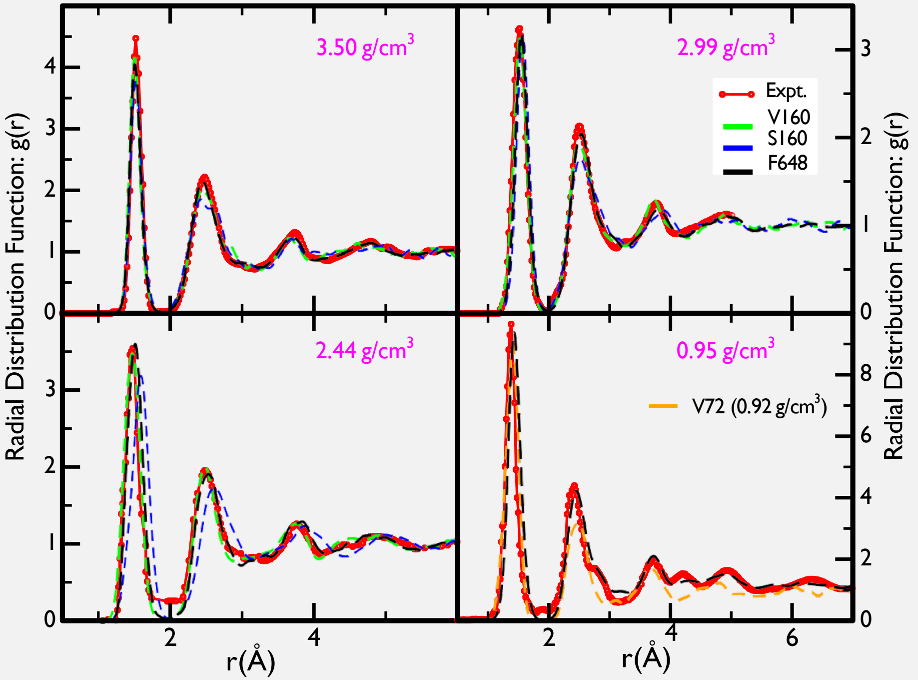


Purple (sp^3), Orange (sp^2), Green (sp)

Bhattarai, Pandey & DAD, Carbon, 131 168 (2018); PCCP 20 19546 (2018)

AMORPHOUS CARBON

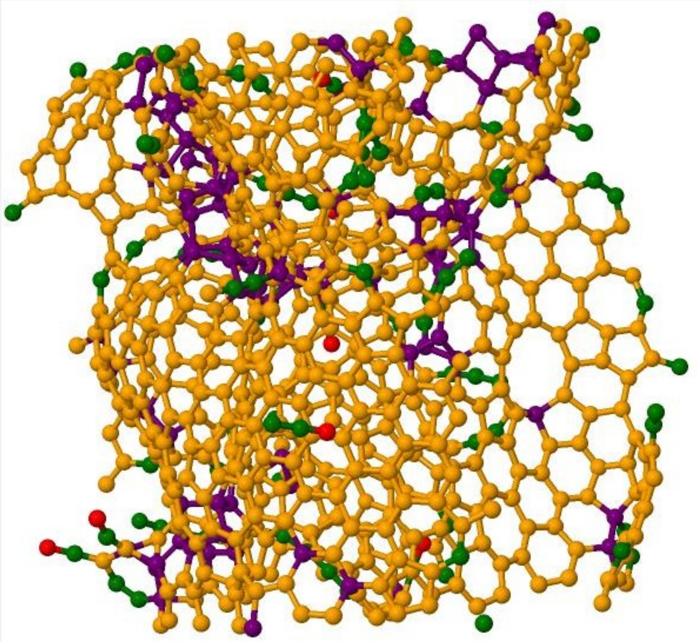


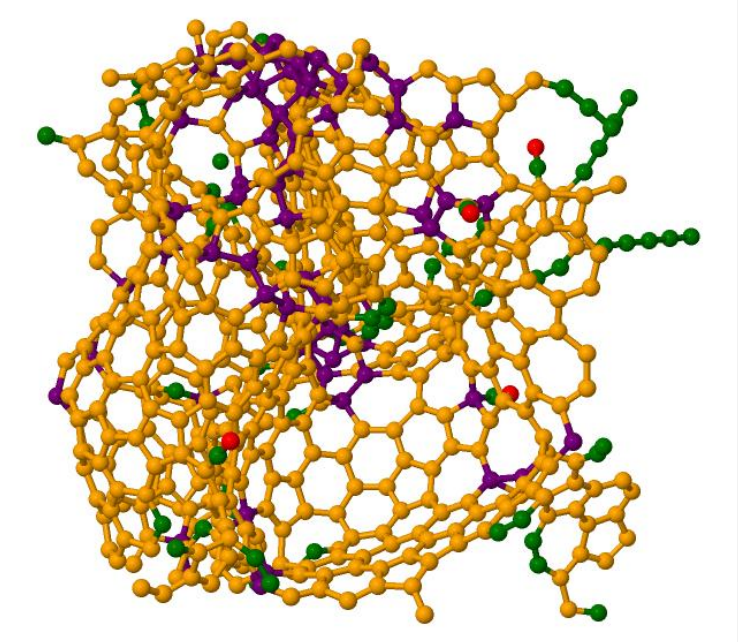


Bhattarai et. al, Carbon (2018)

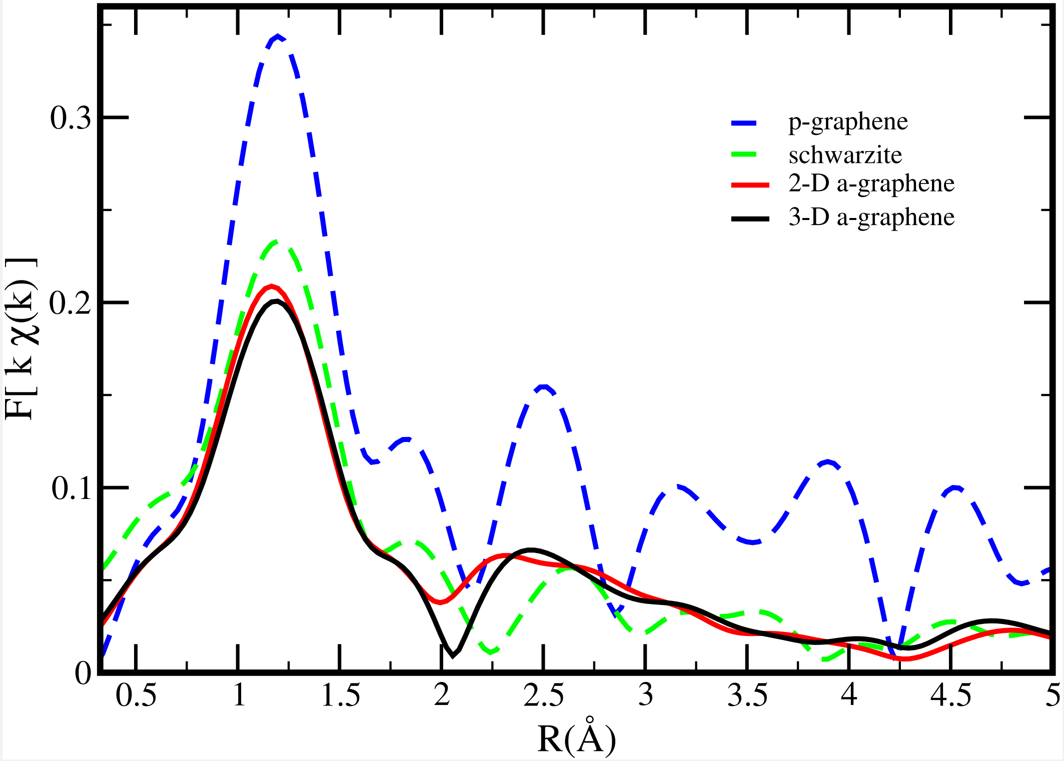
LOW DENSITY (0.95 GM/CC) FEAR CARBON (800-, 648-ATOM MODELS)

Purple (sp^3), **Orange** (sp^2), **Green** (sp)





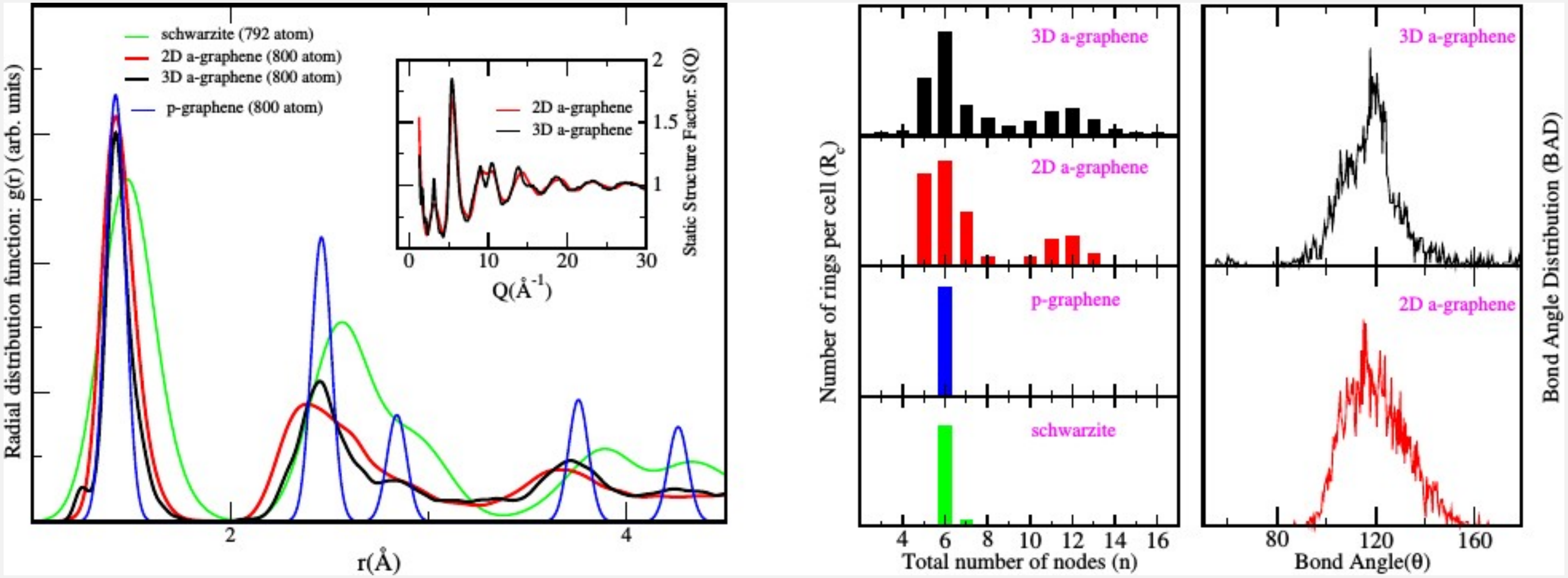
A PREDICTION: EXAFS OF 0.95GM/CC A-C. FAIRLY SMALL DIFFERENCES…



COMMENT

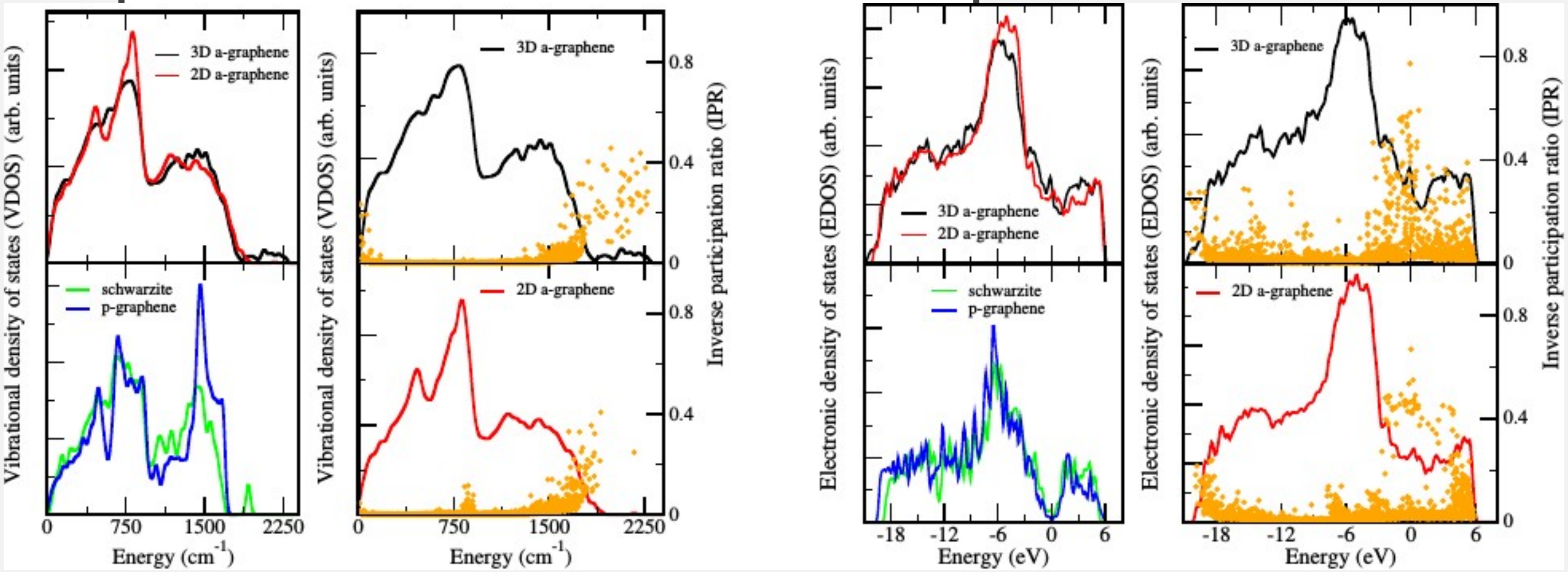
- This computation provides evidence that amorphous C with density near 1 gm/cc is a form of three-dimensional graphene: warped, wrapped sp^2 sheets including ring disorder (pentagons, hexagons, heptagons) and also with sp and sp^3 defects.

STRUCTURAL COMPARISON

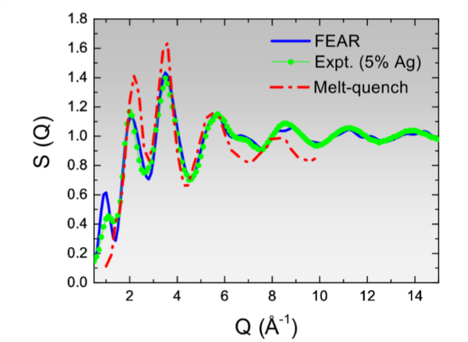


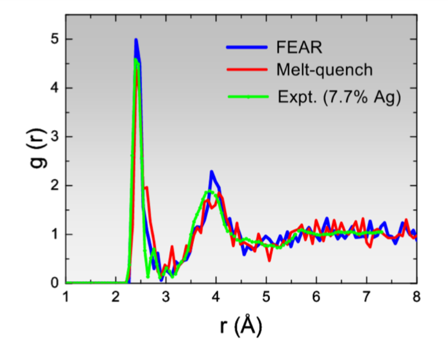
Bhattarai et. al, PRL submitted (2018)

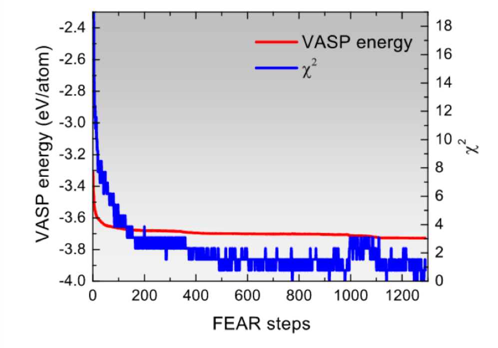
ELECTRONIC AND VIBRATIONAL

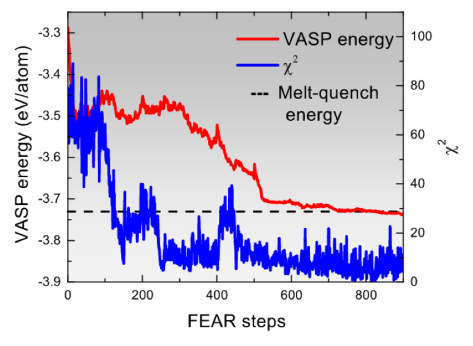


FEAR: AG-DOPED CHALCOGENIDES, $[(\mathrm{GESE}_3)_{1\text{-}X}\mathrm{AG}_X$ X=0.05,0.077] DATA: ZEIDLER AND SALMON (BATH) VASP, A. PRADEL GROUP (MONTPELLIER)









A. Pandey, P. Biswas and D. A. Drabold, *Inversion of diffraction data for amorphous materials, Scientific Reports*, 6 33731 (2016).

CONCLUSION (FEAR)

- Efficient: Fewer calls to force code.

- Robust convergence: Really works [a-Si, a-C (0.95-3.5 gm/cc), GeSeAg materials]. We're trying a metallic glass, fiddling with EXAFS too -- $Pd_{40}Ni_{40}P_{20}$ (nothing to report yet!). Used empirical pots, tight-binding, SIESTA and VASP. Routinely produces (slightly) lower total energies than a reasonable melt quench.

- Dead Easy: if you know RMC and VASP, this is essentially a shell script.