STRUCTURE AND ELECTRONIC PROPERTIES OF AMORPHOUS MATERIALS

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NSF Workshop, Gulfport, MS

PLAN OF LECTURE

- Disorder and Order, introduction
- Electronic structure of amorphous materials
- Note: This is just a quick overview. There are several books. An old (1984) but excellent book is by Elliott, *free for download* on researchgate. You can also have my lecture notes (email me!)
- I am NOT teaching all the lore, only giving the general outlook.

INTERLUDE: SCHRODINGER ON "APERIODIC CRYSTALS"

The non-physicist cannot be expected even to grasp—let alone to appreciate the relevance of—the difference in 'statistical structure' stated in terms so abstract as I have just used. To give the statement life and colour, let me anticipate, what will be explained in much more detail later, namely, that the most essential part of a living cell—the chromosome fibre—may suitably be called *an aperiodic crystal*. In physics we have dealt hitherto only with *periodic crystals*. To a humble physicist's mind, these are very interesting and complicated objects; they constitute one of the most fascinating and complex material structures by which inanimate nature puzzles his wits. Yet, compared with the aperiodic crystal, they are rather plain and dull. The difference in structure is of the same kind as that between an ordinary wallpaper in which the same pattern is repeated again and again in regular periodicity and a masterpiece of embroidery, say a Raphael tapestry, which shows no dull repetition, but an elaborate, coherent, meaningful design traced by the great master.

E. S. "What is Life" (lectures in Dublin from 1942). p. 3 of the 1962 CUP reprint

MOTIVATION

- To understand disordered matter via computer models.
- To design materials with sought after properties.

Fact: neither experimentalists nor theorists succeed by themselves in our field – it's all about working together.

DISORDER: SCOPE OF THE PROBLEM

THE CHALLENGE

- All solids are fundamentally quantum mechanical entities: we know that lattice vibrations have to be quantized, accurate forces come only from quantum mechanics, can only understand metals and insulators with quantum mechanical electrons, etc.
- The structure of amorphous solids is unknown and always will be in a literal sense**: no experiment can tell us $\mathbf{10^{22}}$ coordinates and no computer can store them**.
- So we will need a way to make **representative** atomic models and deal with quantum mechanics in such an extended, disordered system.

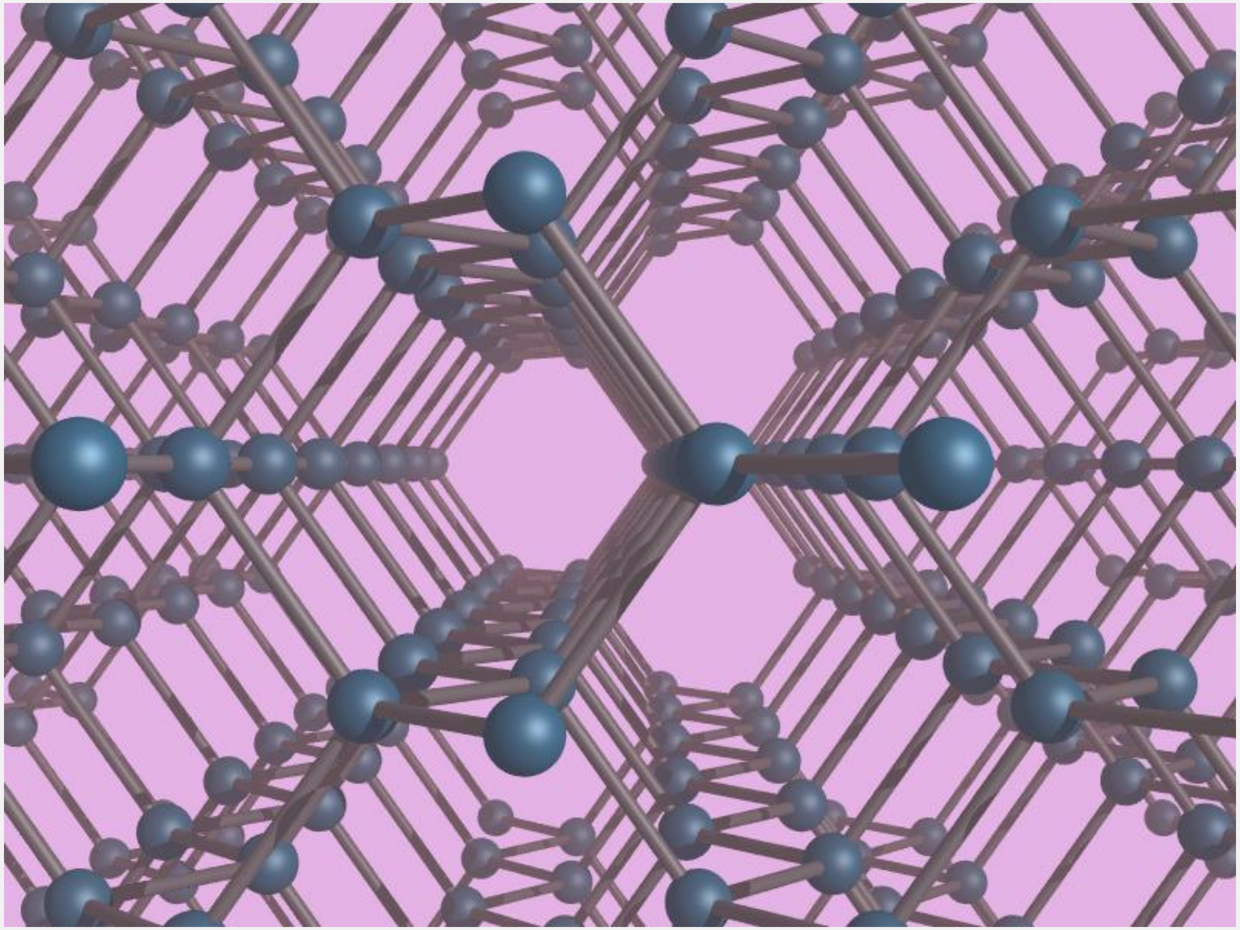
WHAT WE KNOW: CLUSTERS

- We can work out the properties of molecules pretty well with standard methods.
- Number of energy minima grows exponentially with number of atoms (Stillinger). Finding the "ground state" becomes difficult before even 20 atoms. A harbinger of challenges ahead…
- No k-space, no bands etc, just molecular orbitals.
- Not usually a good way to represent a solid – surface artifacts.

WHAT WE KNOW: CRYSTAL

- Crystal: a configuration of atoms arrayed in periodic fashion.
- Can come with one atom per unit cell (Bravais lattice FCC, BCC, SC etc), or there may be a *basis* (a collection of translations) associated with each point in a Bravais lattice (for example, diamond). Or 10^6 atoms – proteins. Most recent Nobel prize: 2009.

DIAMOND



WHY CRYSTALS ARE EASY: SYMMETRY AND ITS USE

- The basic point is: we know where the atoms are**,** and their **periodicity** has important consequences.
- For calculations, the periodicity makes a critical difference. Since the electronic or vibrational Hamiltonian commutes with the translation operator, we get Bloch's theorem:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}).$$

u has full periodicity of the lattice, (*n**k***) labels the electronic states

CRYSTALS ARE EASY

- Bloch's theorem lets us work with two indexes: n, the band index and **k**, the Bloch wave-vector. For a macroscopic system, **k** continuous, all information is included first Brillouin zone.
- In calculations, we can solve

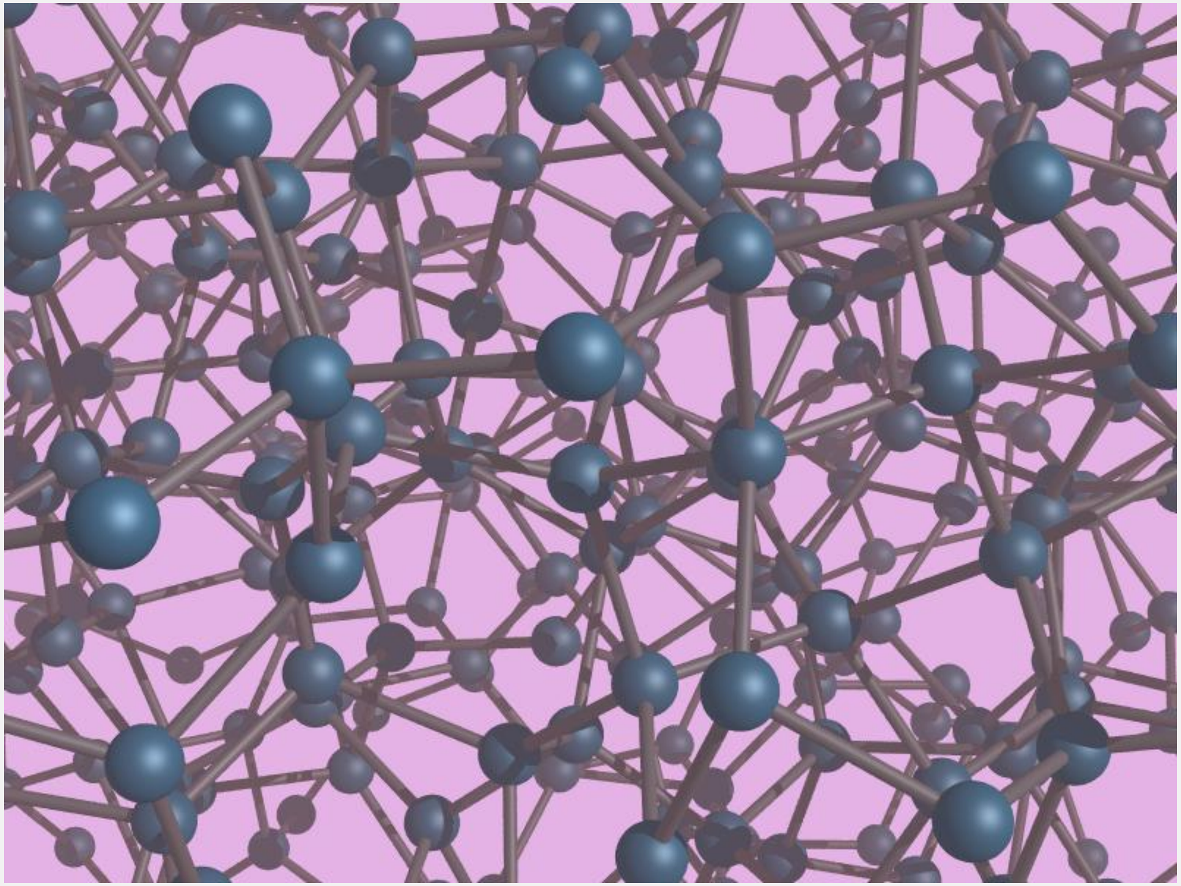
$$H(k)\ \psi(n,k)=E(n,k)\ \psi(n,k)$$

We solve this independently for each k. We diagonalize a matrix of dimension N_{basis} where N_{basis} is of order the number of valence electrons per site, **not** of order the number of atoms!

CRYSTALS ARE EASY: II

- Diffraction experiments for xtals give sharp peaks. From these it is possible to uniquely infer the structure (essentially, invert the experiment). **The Bragg problem.**
- Disorder gives smooth functions with a few. peaks Vastly less information in the diffraction experiment. **Impossible** to "invert" the experiment without additional information.
- Very similar statements are true for lattice vibrations.

OUR PROBLEM: DEALING WITH THIS!



DISORDER IS CHALLENGING

- It's difficult to even work out "representative" coordinates.
- Even with the coordinates, "post processing" (like studying electronic structure) scales much worse with N (depending on the method)
- We would like to get ground state properties, transport, and some information about excitations (as for optics).
- We lose Bloch's theorem.

ROLE OF EXPERIMENT: STRUCTURE

- For amorphous materials we have a variety of probes:

Scattering: X-rays, neutrons etc (averaged, so extremely incomplete) “sum rule”

Electronic and optical (indirect, and averaged)

NMR, etc (indirect and averaged)

STM (even *if* it can be done as a surface probe)

EXPERIMENT MUST BE COMPLEMENTED BY MODELING TO GAIN UNDERSTANDING

- Hope is that adding what we know from experiment to theory will yield a "complete" picture.
- To make any progress at all on electrons, phonons, optics or transport we must have a structural model
- **Therefore the overarching problem of this field is structure determination.**

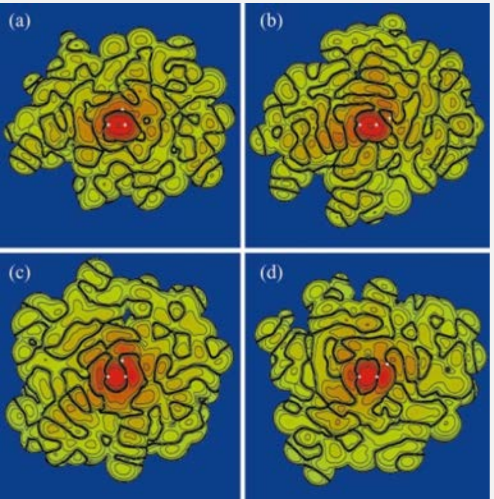
STATE OF THE FIELD

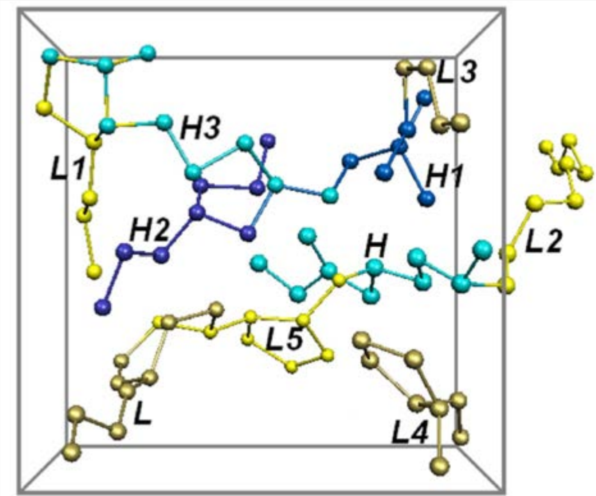
- New experiments: Ever more brilliant X-ray sources, a number of facilities for elastic and inelastic neutron scattering. STM is advancing.
- New theory: A revolution in the last 20 years – realistic atomistic models of disordered systems. Ever-improving quantum mechanical simulation codes and Machine Learning.
- New applications: photovoltaics (a-Si:H), batteries (solid electrolytes), computer memory devices (DVD, CD, solid state FLASH – phase change and conducting bridge). TFTs, fiber optics, night vision………

BASIC SCIENCE: SOME OPEN QUESTIONS

- Structural estimation/prediction/inference
- Engineering the properties we want (MGI)
- Metallic glasses and quasicrystals (Nobel: Schectman; ribbon quench)
- The nature of electron states and transport in disordered materials (Nobel: Anderson and Mott). Localization has taken on a life of its own (Ball Lightning!!)
- Weird low-T specific heat, "tunneling modes". The key to LIGO!
- Computer memory devices made with solid amorphous electrolytes
- *Many others….*

ELECTRONS IN DISORDERED MATERIALS





ROADMAP

I. A simple picture of the Anderson transition.

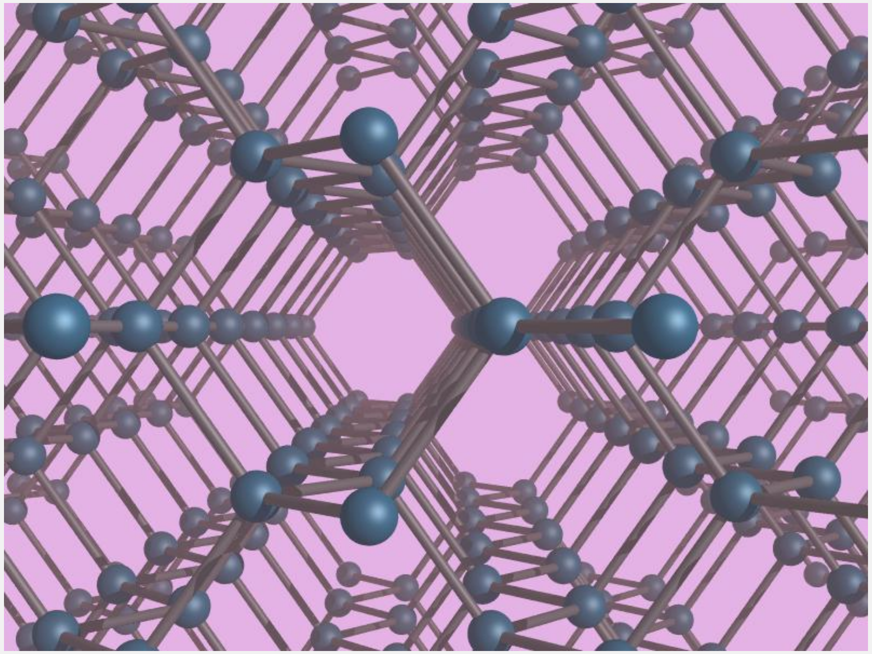
II. Non-locality of quantum mechanics in the solid state -- with disorder.

III. The coupling to phonons.

Implement this for real materials using credible models.

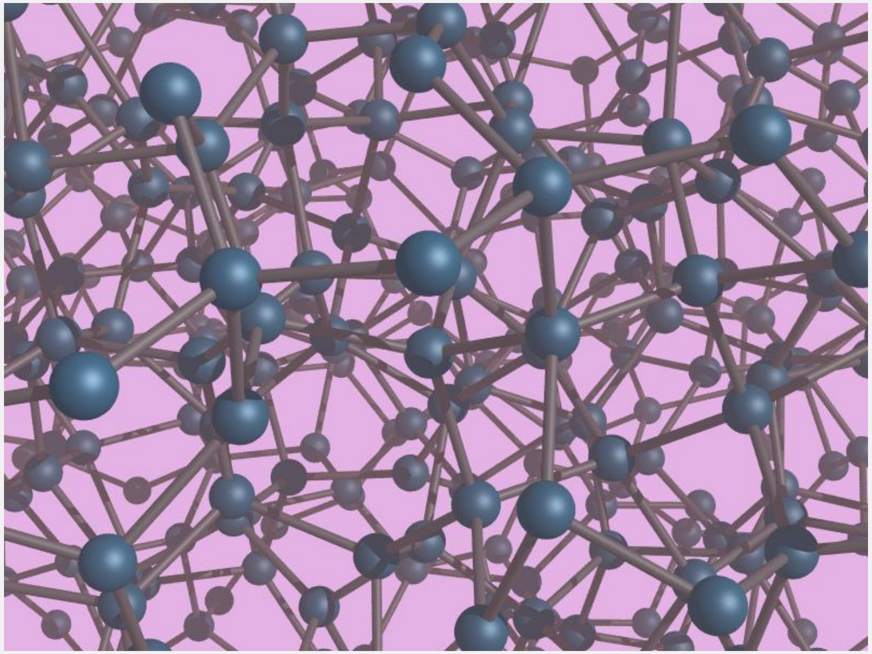
Q. *How does disorder in atomic coordinates affect the electron states?*

Crystalline Si (diamond)



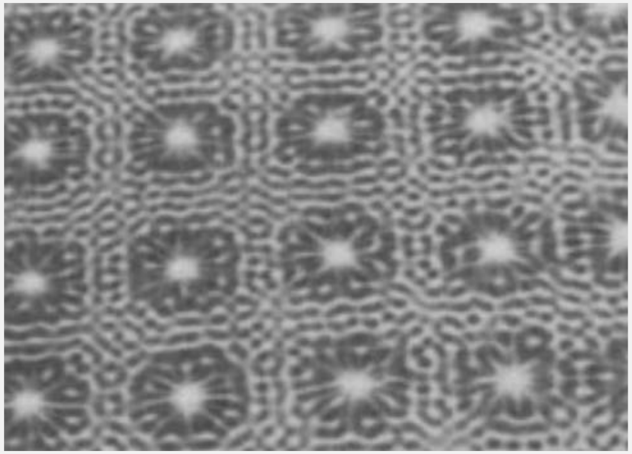
Translational periodicity
Bloch states

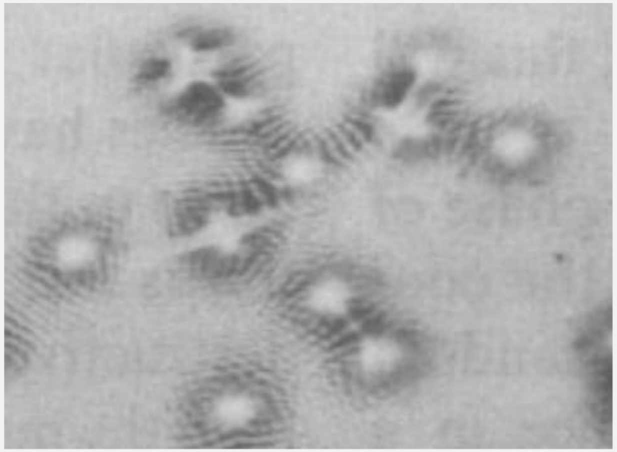
Amorphous Silicon



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

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

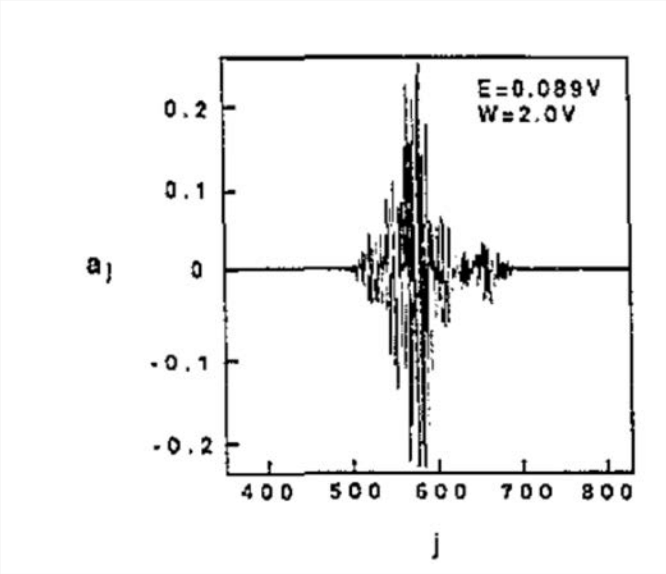
E_I are random, "diagonal" disorder. Fact -- enough variation in E_I -- all states localized!

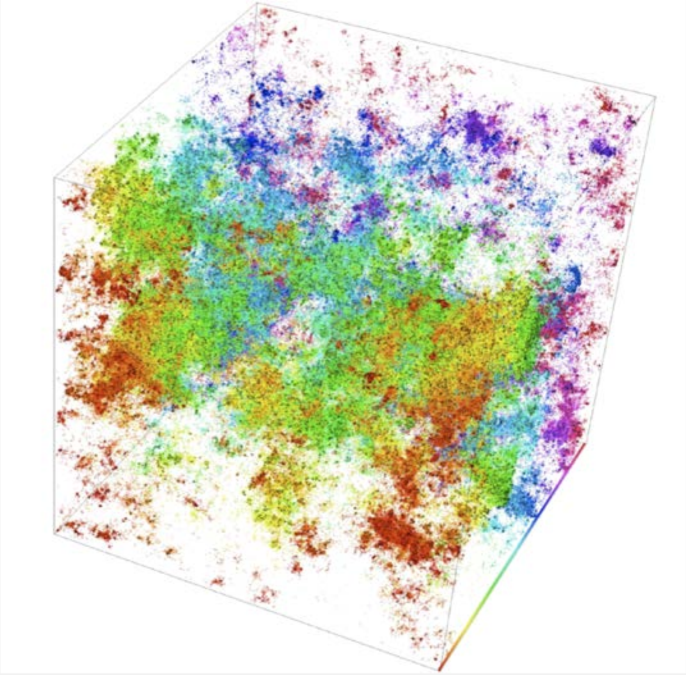
Topological (bond length/angle) disorder
$H = \sum_I |I><I|\, E_I + \sum_{IJ} |I><J|\, S_{IJ}$

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

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

ANDERSON MODEL



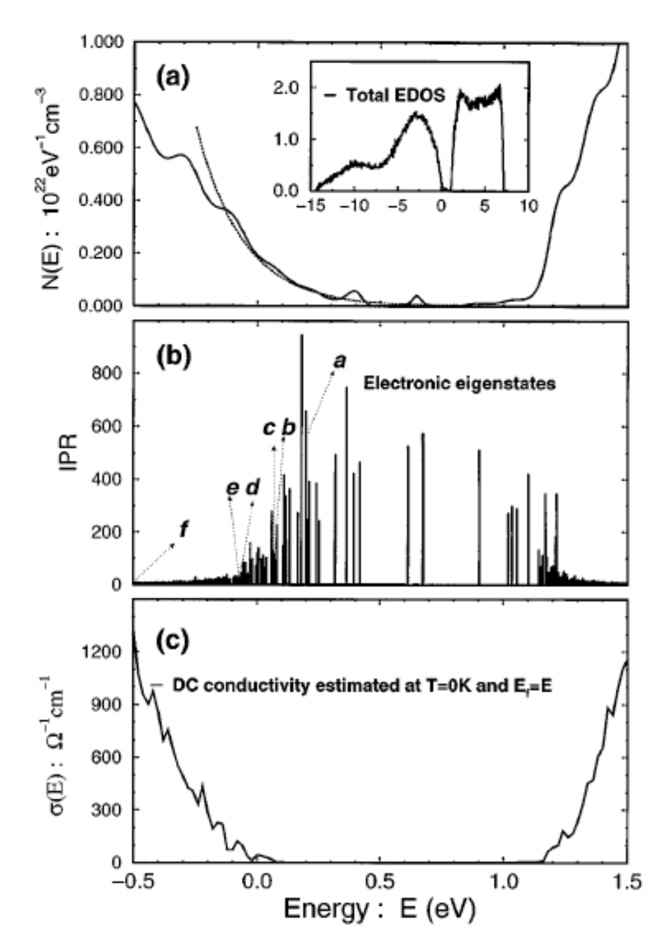


Left: A localized eigenstate in 1D (Kramer/MacKinnon)
Right: 3D critical eigenstate (15.6M sites; Roemer)

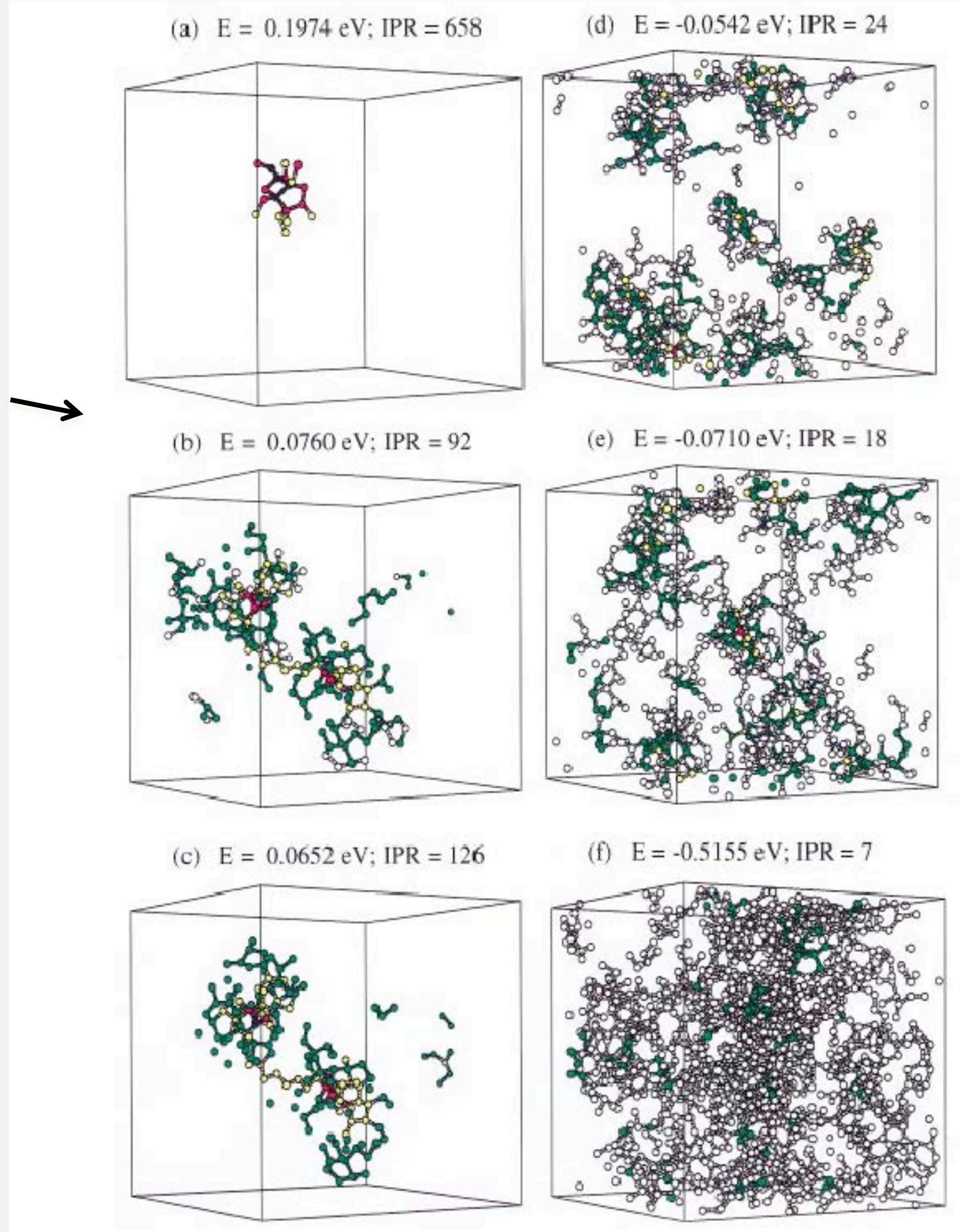
I. APPROACH FOR A REAL MATERIAL

- 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

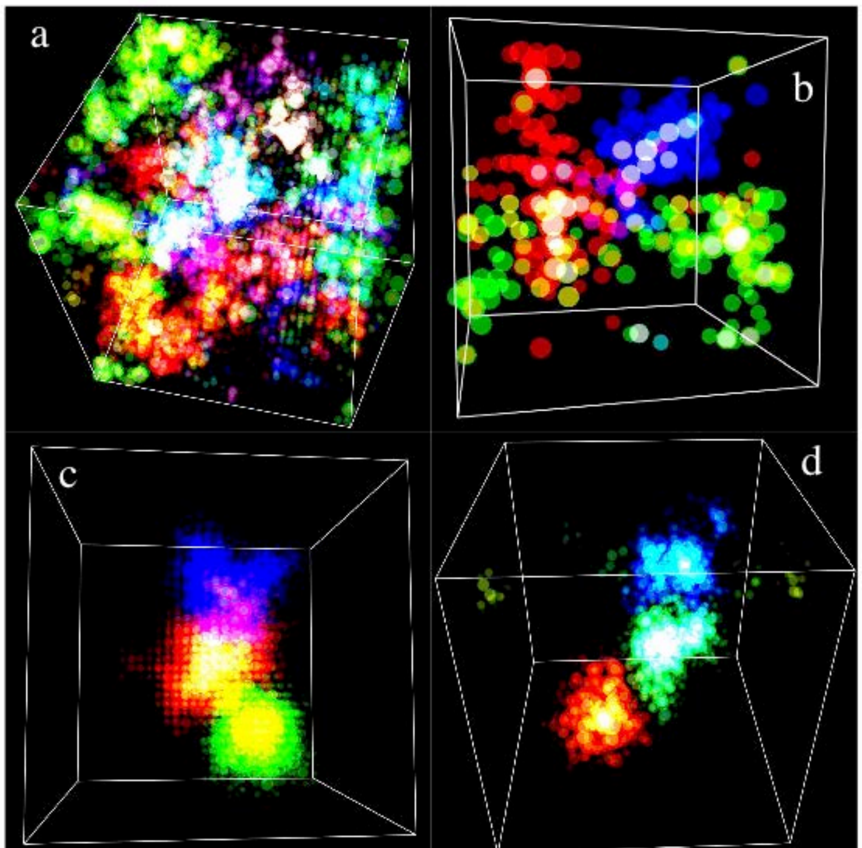
- Structural irregularities or defects "beyond the mean" exist.
- If "bad enough" these induce localized wave functions.
- If two such defects are spatially near and have similar energies, system eigenstates will be mixtures. "States b and c" [clue: Symmetric and anti-symmetric linear combinations of 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).

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

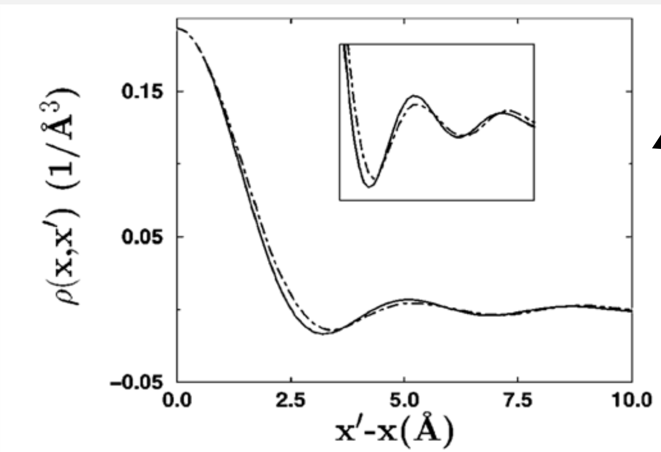
$$\rho(\mathbf{x},\mathbf{x}') = 2 \sum_{n\ \mathrm{occ}} \psi_n^*(\mathbf{x})\, \psi_n(\mathbf{x}')$$

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

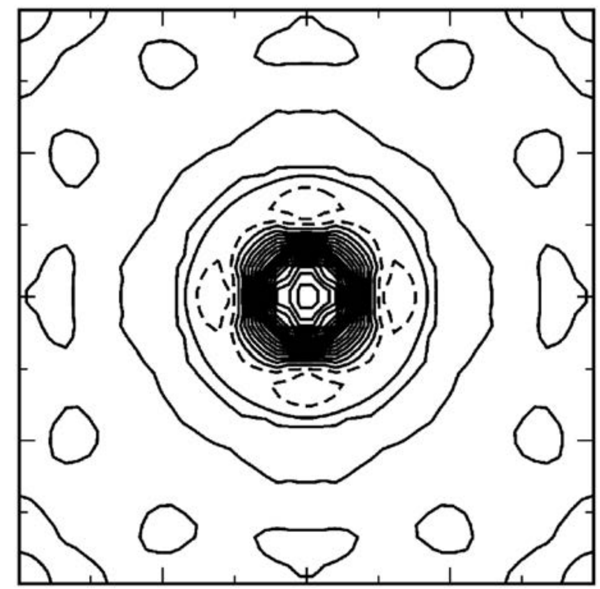


FIG. 4. Contour plot of the real-space density matrix for Al calculated in the {100} plane for the conventional cubic unit cell (the x-y axes are parallel to the bonds).

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)

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

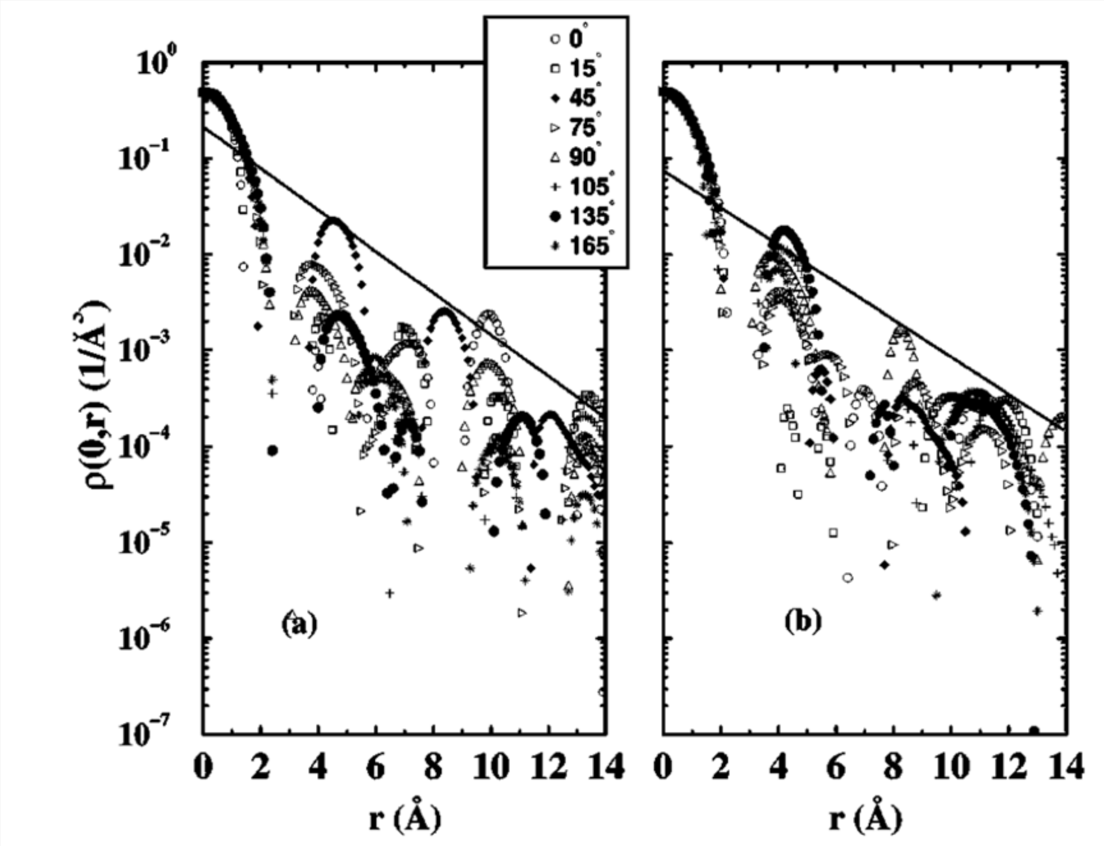
S is a (known) sum, depending on dimensionality D=1,2,3

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

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

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

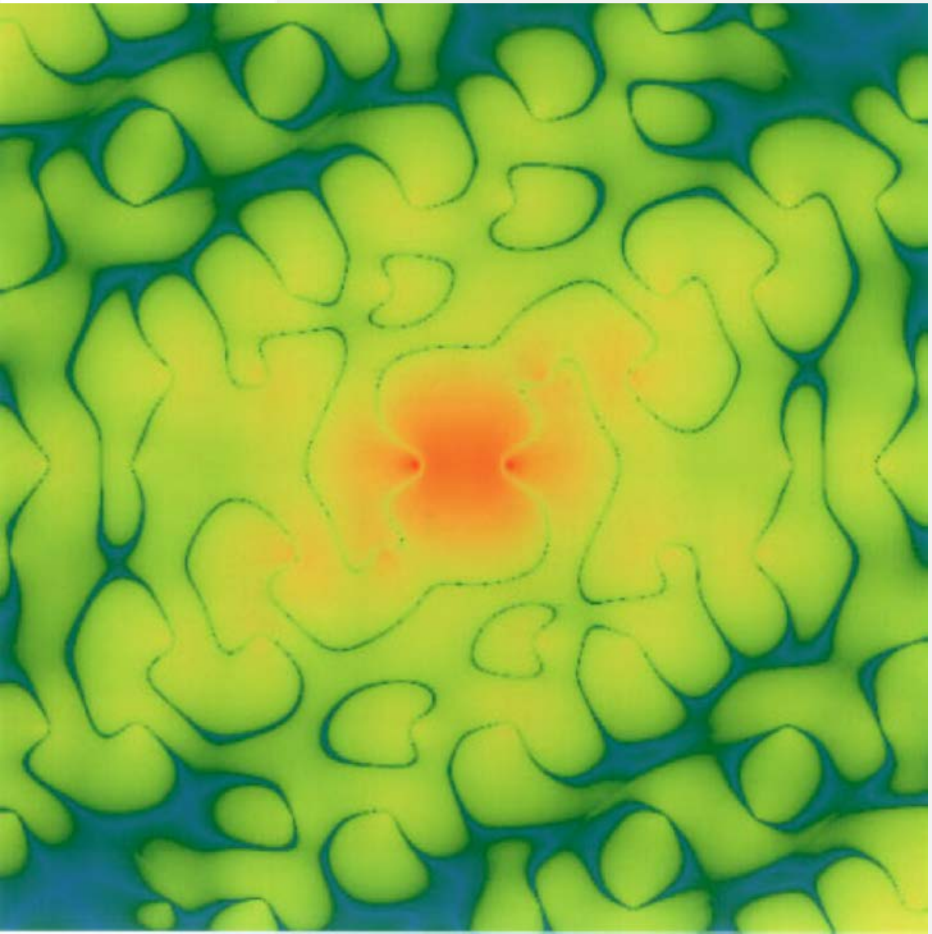
- Wannier functions: unitary transformations of eigenstates localized in real space.
- Not unique, *but* Vanderbilt showed how to compute maximally-localized Wannier functions[1].
- Long range decay of these is similar for c-Si and a-Si, and similar to decay of density matrix.
- We compute with an O(N)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

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

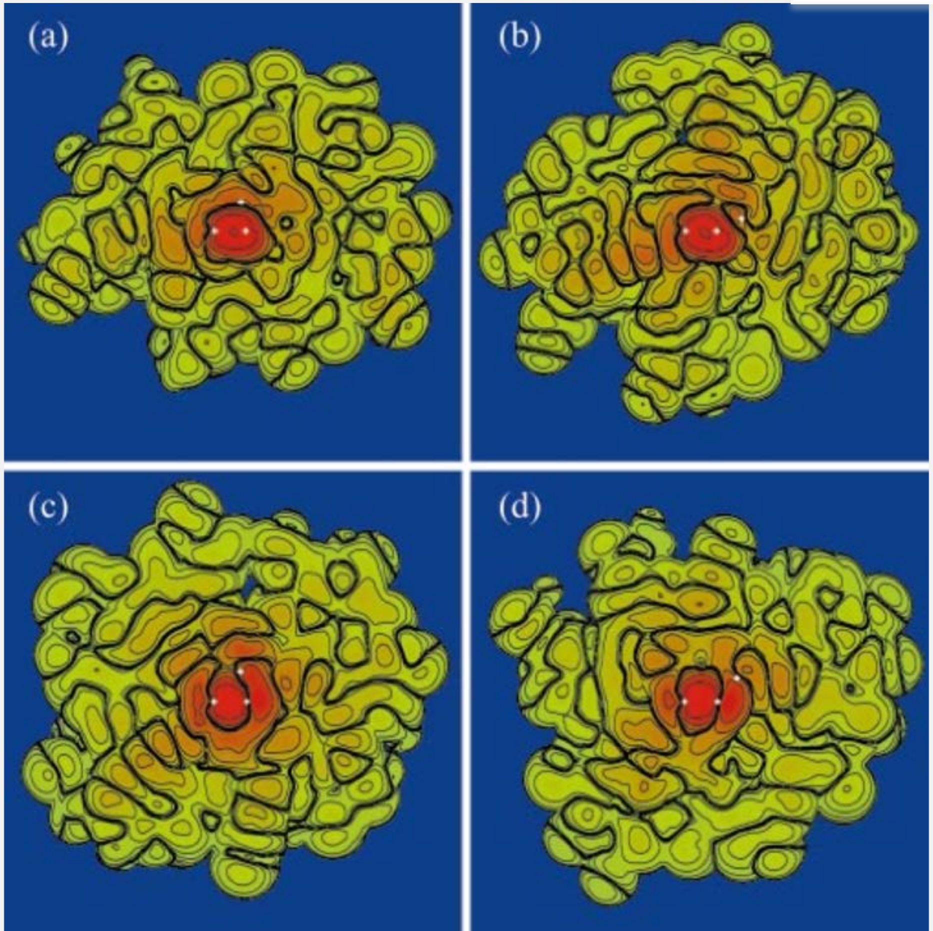
WANNIER FUNCTIONS FOR DISORDERED SYSTEMS

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

Diamond



a-Si



CONCLUSION: LOCALITY

We quantify Kohn's Principle:

(1) Analytically for two-band insulator

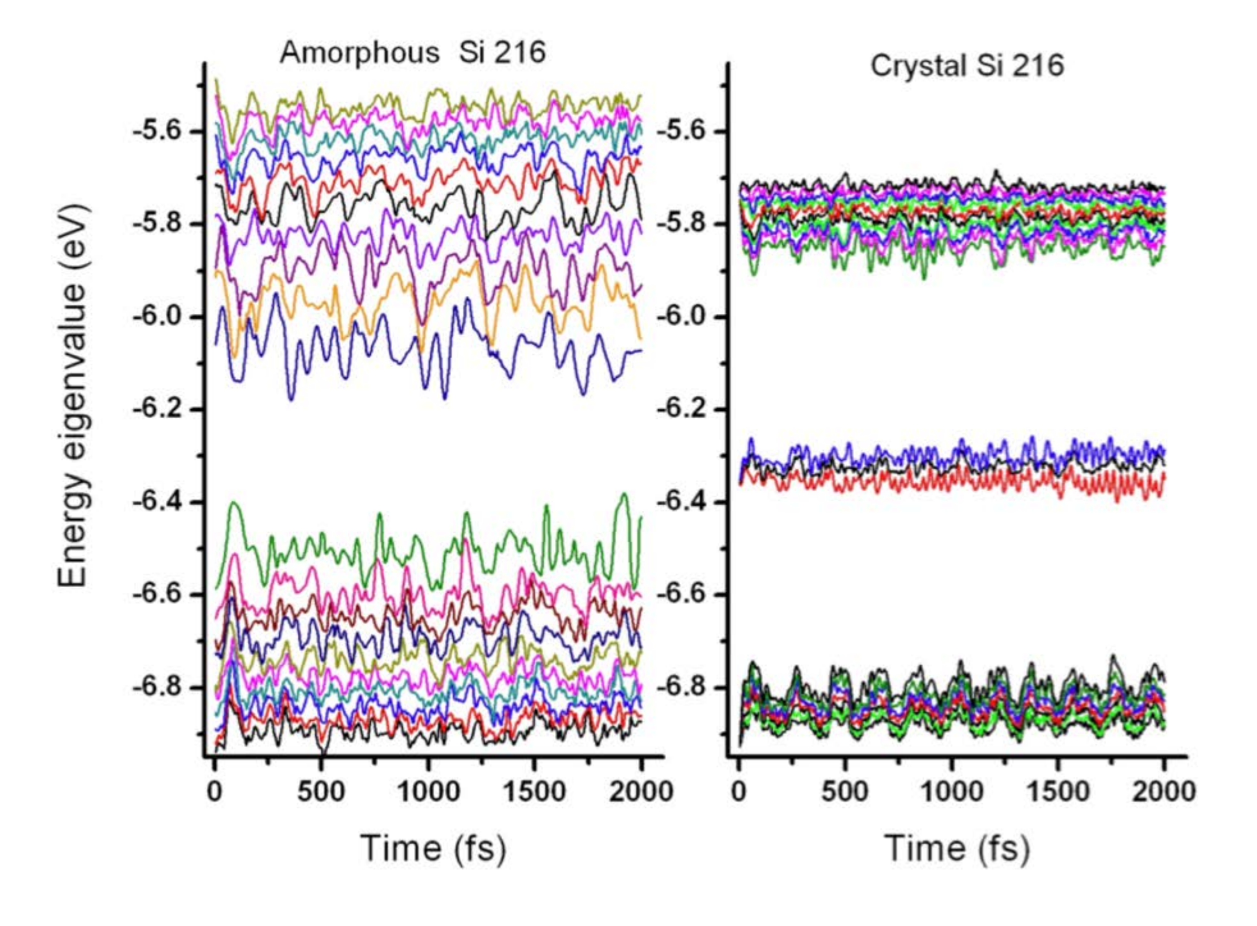
(2) By direct calculation of ρ with Kohn-Sham orbitals for metals, crystalline and amorphous semiconductors. Also Wannier functions from projection.

(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

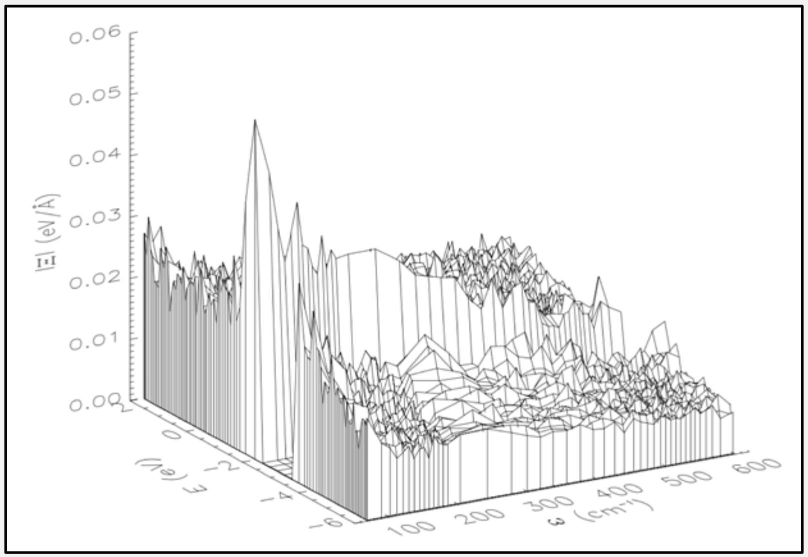
- Hellmann-Feynman theorem and harmonic approximation with classical lattice dynamics leads easily to fluctuations in electron energy eigenvalue $\langle\delta\lambda^2\rangle$:

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

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

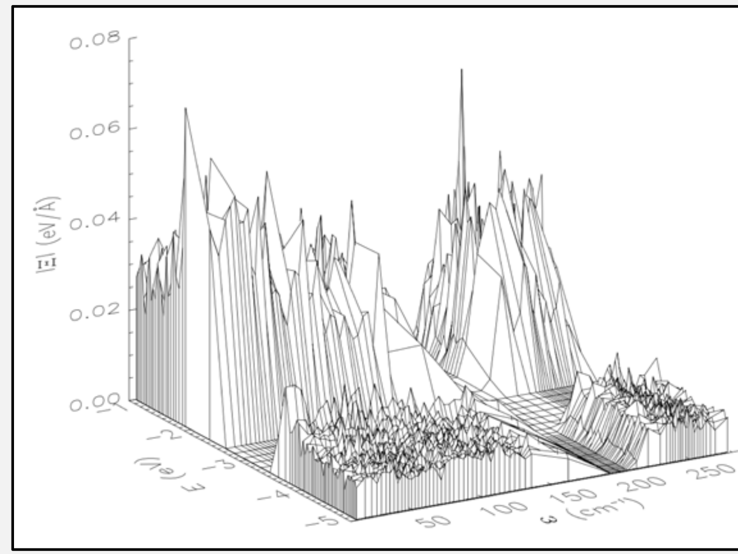
We call Ξ the electron-phonon coupling

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



Si

Se



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

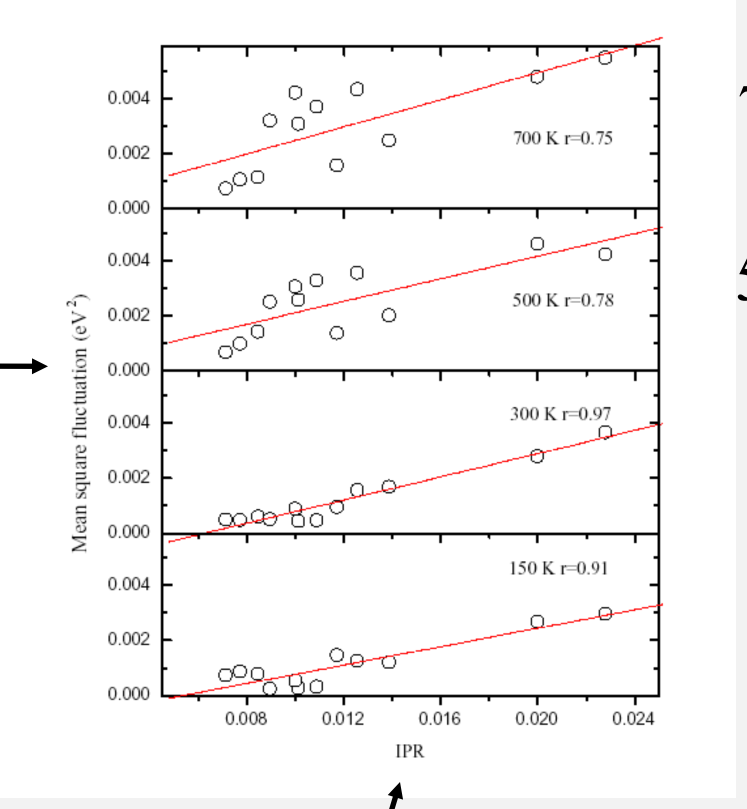
Couple electron n (energy E) and phonon ω

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

CORRELATION BETWEEN LOCALIZATION AND THERMAL FLUCTUATION FROM MD

$<\delta\lambda^2>$

(T>0 property)



700K

500K

300K

150K

Fits analytic result for low T

Localization (T=0 property)