Computing electrical conduction pathways in materials

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Thermoelectrics group talk, 2024

Computing the electrical conductivity of a computer model of a material

- Electrical conductivity is a key observable. It is however just a *number* (for the DC conductivity) or a function $\sigma(\omega)$ for the AC case.
- The tool to compute $\sigma(\omega)$ is the "Kubo formula". From the quantum mechanics of a material (wave functions, energy eigenvalues -- computed in any modern *ab initio* simulation) it returns $\sigma(\omega)$.
- Conduction arises from quantum transitions near the Fermi level (for the AC case) and *at* the Fermi level for the DC case.

$$\sigma_{\alpha\alpha}(\omega) = \frac{2\pi e^2\hbar}{\Omega m^2}\sum_{ni} |\langle\psi_n|p_\alpha|\psi_i\rangle|^2 \frac{f_F(\varepsilon_i) - f_F(\varepsilon_n)}{\hbar\omega}$$

$$\times\ \delta(\varepsilon_n - \varepsilon_i - \hbar\omega),$$

Single-particle form:
"Kubo-Greenwood" formula
Kubo (1957), Greenwood (1958), Mott, (1960's).

But there is a wider world

- In this talk we extract atomistic information about *conduction mechanisms.* We determine transport processes in the material: which atoms, or microstructures contribute to the conduction, how much, etc.
- The method is readily implemented for any current DFT code (we used VASP).

- Some notable previous work:

R. B. S. Oakeshott, A. MacKinnon, *Journal of Physics: Condensed Matter* 1994, 6, 8 1513.

H. U. Baranger, A. D. Stone, *Phys. Rev. B* 1989, 40 8169.

The rest of the talk

- In the next few slides I show how to ”deconstruct” the Kubo-Greenwood formula to obtain spatial information about conduction.
- Basic idea is to tear it apart (and reassemble it) in a form that conveys spatial information about transport.
- And we then apply it to interesting (?) examples…

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

i,j: Kohn-Sham or other single-particle states, **k** Bloch vector, α Cartesian index
p: momentum operator.

So by direct substitution:

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

Define complex-valued functions on grid points in space **{x}**:

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

Write the conductivity as a discrete spatial sum (suppose uniform grid spacing in 3D, call it *h*), so….

$$\sigma \approx h^6 \sum_{\mathbf{x},\mathbf{x}'} \sum_{ij\alpha} g_{ij} \xi_{ij}^{\alpha}(\mathbf{x}) [\xi_{ij}^{\alpha}(\mathbf{x}')]^*$$

Define the Hermitian, positive-semidefinite matrix

$$\Gamma(\mathbf{x},\mathbf{x}') = h^6 \sum_{ij\alpha} g_{ij} \xi_{ij}^{\alpha}(\mathbf{x}) [\xi_{ij}^{\alpha}(\mathbf{x}')]^*$$

Call Γ "the conduction matrix"

Then:

$$\sigma = \sum_{\mathbf{x},\mathbf{x}'} \Gamma(\mathbf{x},\mathbf{x}')$$

So the natural spatial projection is:

$$\zeta(\mathbf{x}) = \left| \sum_{x'} \Gamma(\mathbf{x}, \mathbf{x}') \right|$$

In general the sum is complex. Hence the absolute value bonds.

Eigenmodes of conductivity:

diagonalize Γ in position representation

$$\hat{\Gamma} = \sum_{\mu} |\chi_\mu\rangle \Lambda_\mu \langle\chi_\mu|$$

Λ has units of conductivity, and:

$$\sigma = \sum_{\mu} \Lambda_\mu + \sum_{x,x',x\neq x'} \sum_{\mu} \Lambda_\mu \chi_\mu(x) \chi_\mu^*(x')$$

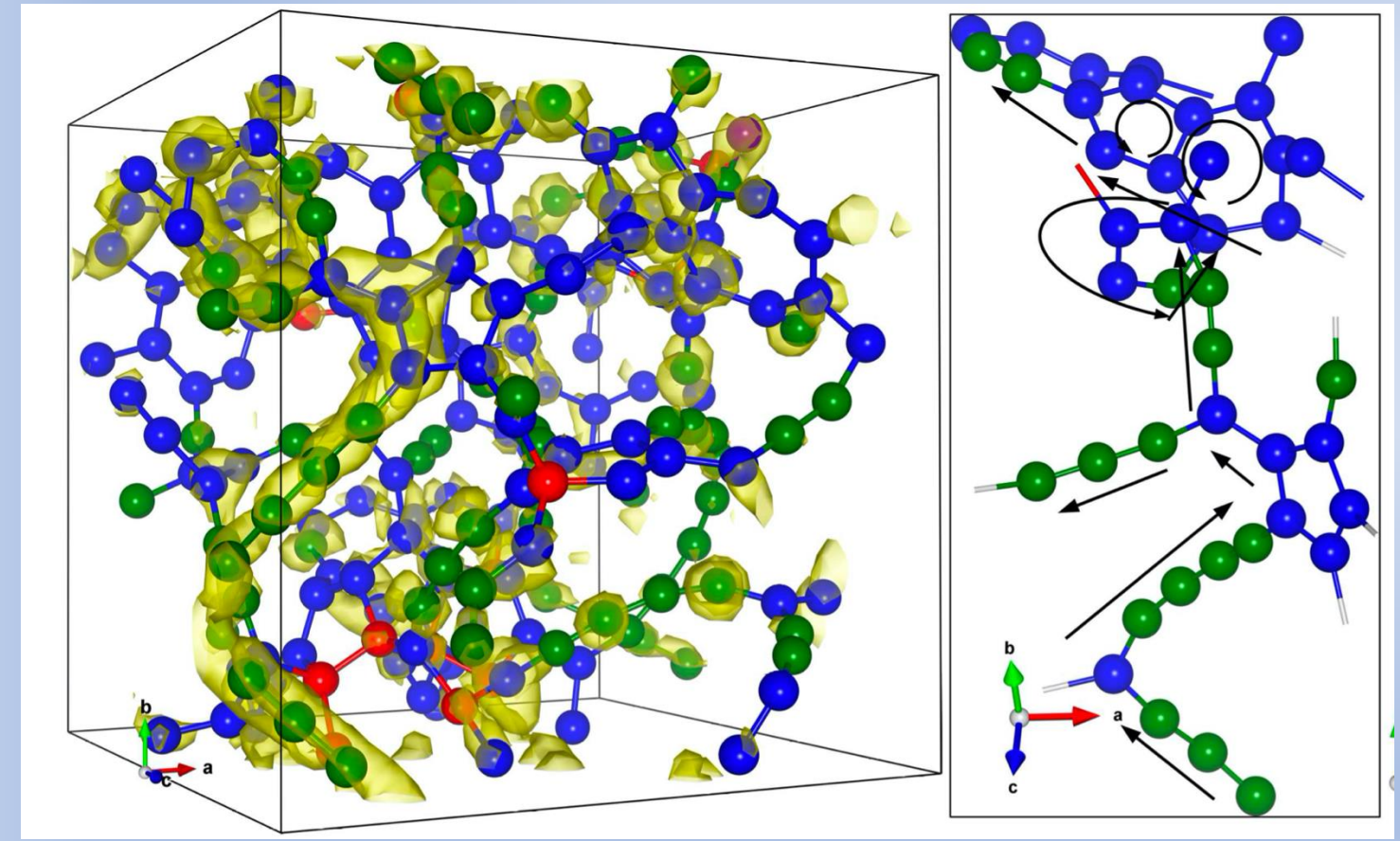
The eigenvectors pick out the key 'paths'. In practice, we require a small fraction of the spectrum.

$$\zeta_s(\mathbf{x}) = |\sum_{\mu} \Lambda_\mu \{|\chi_\mu(\mathbf{x})|^2 + \sum_{\mathbf{x}',\mathbf{x}' \neq \mathbf{x}} \chi_\mu(\mathbf{x})\chi_\mu^*(\mathbf{x}')\}|$$

[From completeness $\zeta_s=\zeta$ if we include all μ]

"*Mapping the computation of percolating paths to a diagonalization*" (J. C. Phillips, 2019).

Examples: (1) low density a-C (1.5 gm/cc)



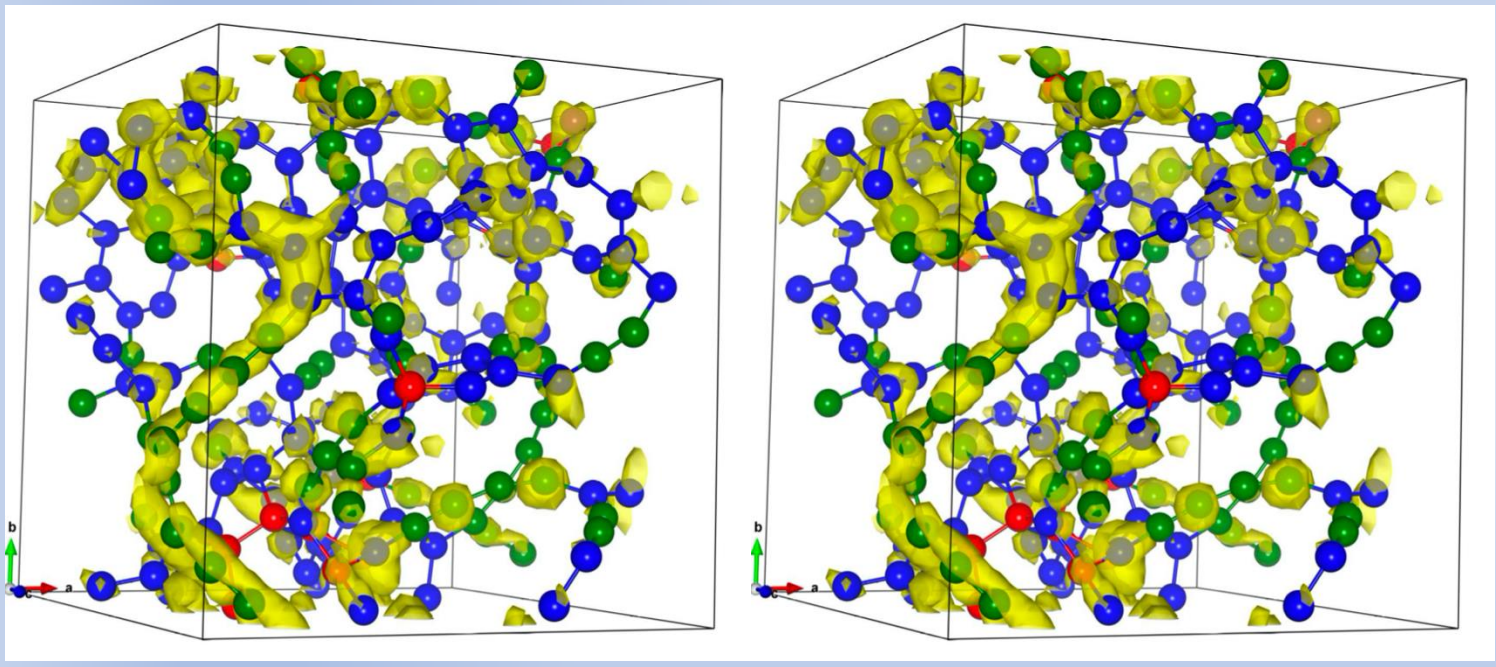
Red: sp^3, blue sp^2
green: sp. Flaxen haze is $\zeta(\mathbf{x})$.

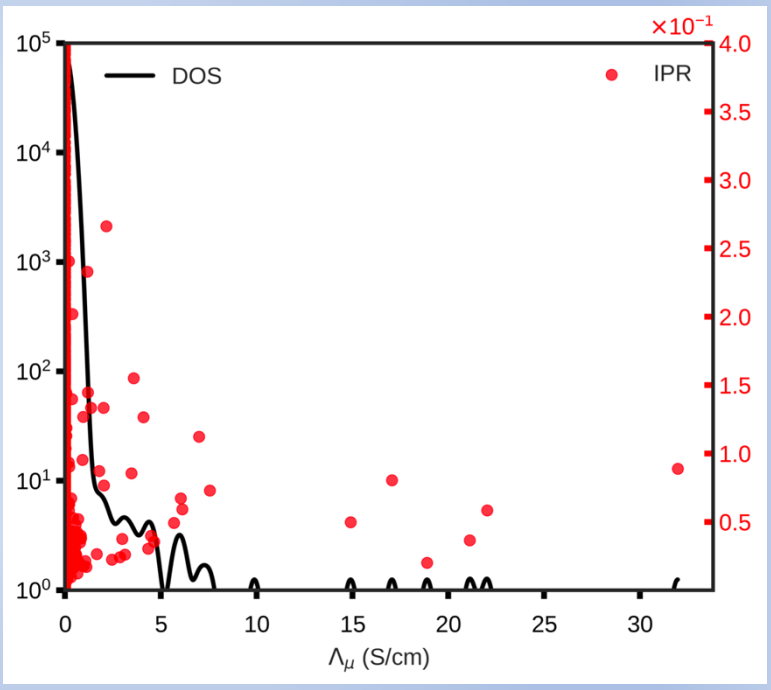
Conduction is via sp chains connected with sp^2 rings.

Thanks to Felix.

Model: B. Bhattarai *et al.*, *Carbon* 131 168 (2018).

Spectral representation: a-C





Sum on 100 eigenvectors

Note: dim(Γ)=64,000

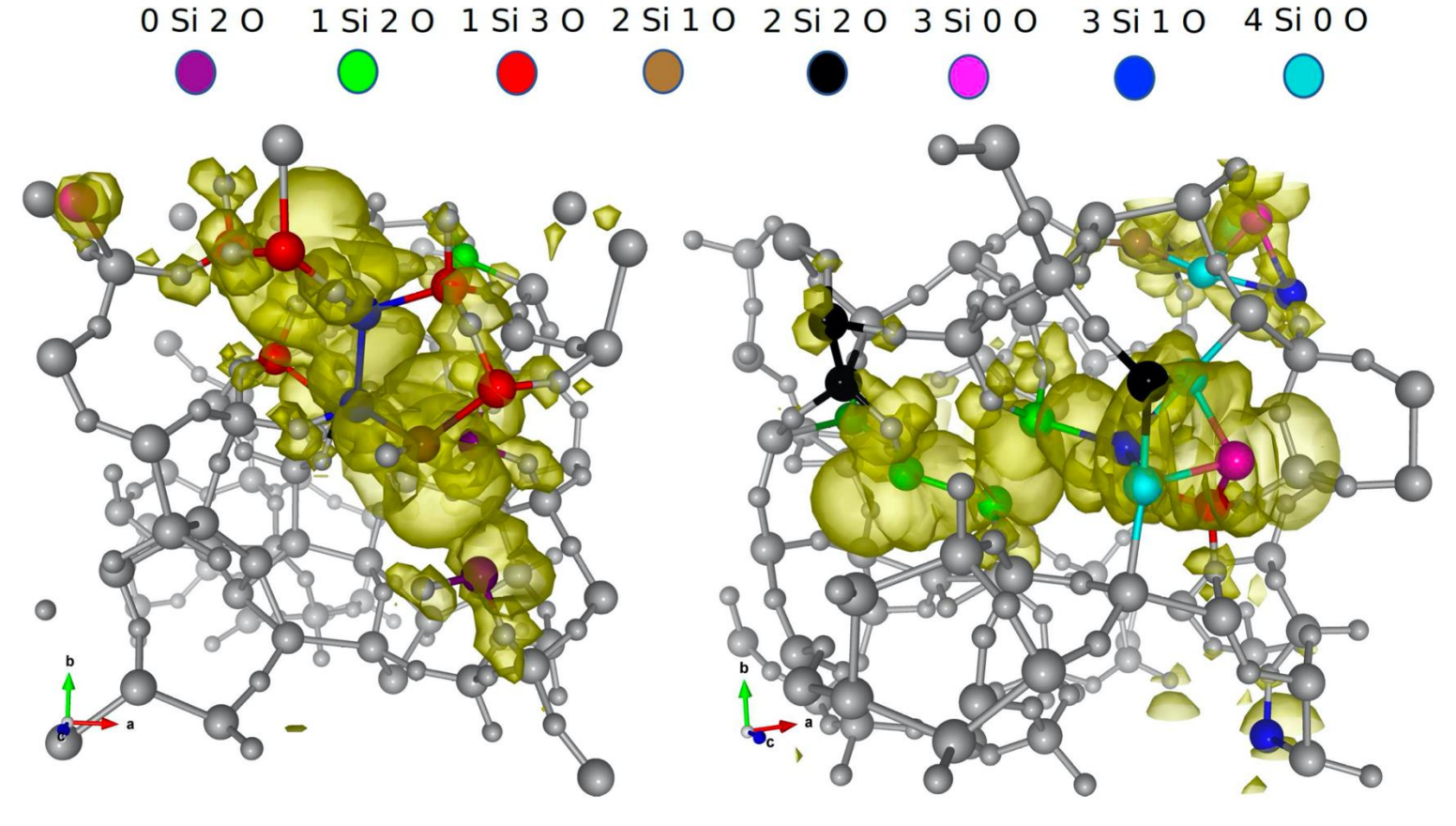
Exact $\zeta(\mathbf{x})$

Log density of states of Γ, IPR

Example (2): Finite frequency: which atoms absorb light at what wavelength?

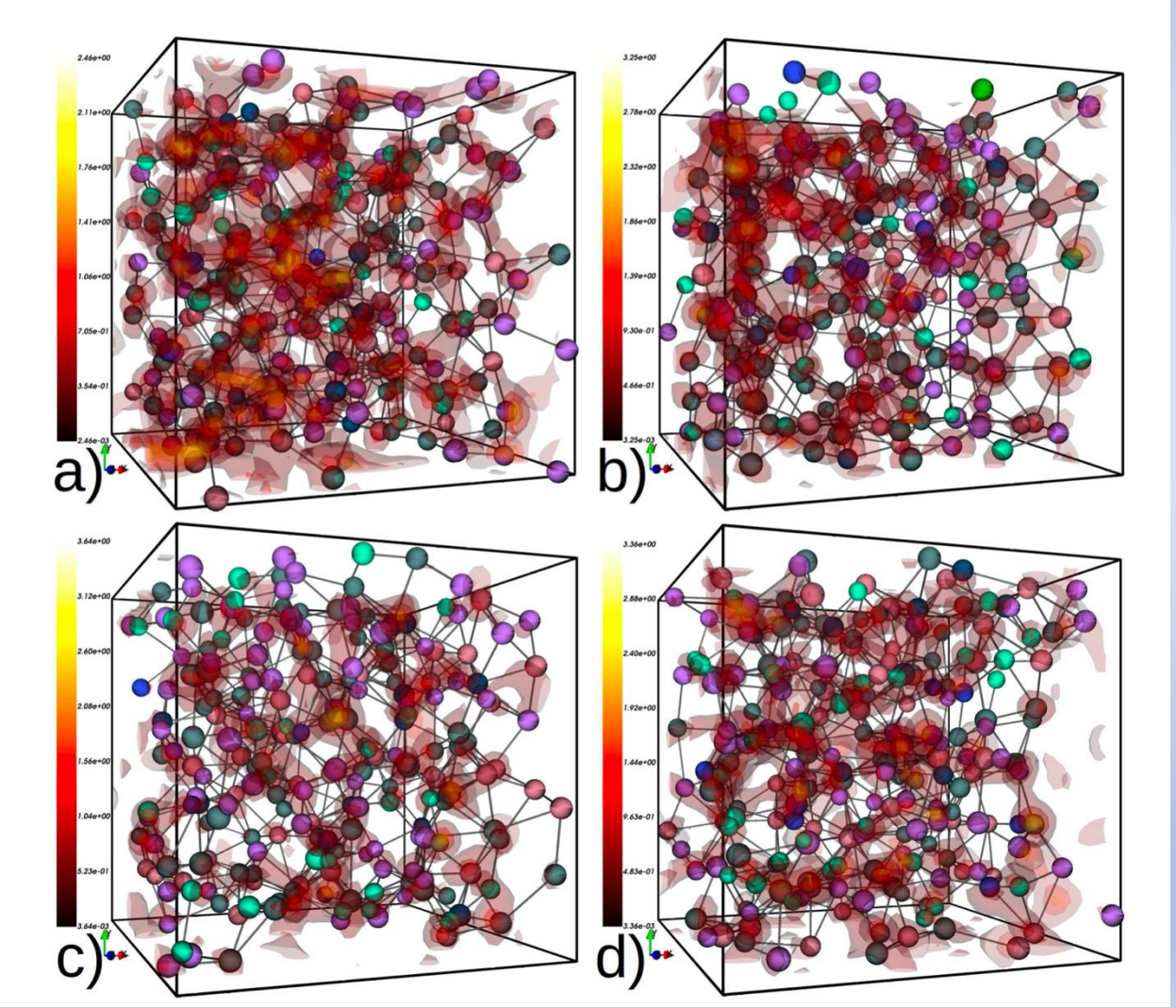
- Here we look at a model of an amorphous silicon suboxide: a-$SiO_{1.3}$.
- For a 'severely O depleted' a-SiO_2 network, transport is through O vacancies and perhaps other defects.
- If we shine light at two different wavelengths (λ=2000 nm and λ=1600 nm), what parts of the material absorb the light in the two cases?
- Note: applied interest for computer security applications: Physically Unclonable Functions (M. N. Kozicki!).

Absorption: λ=2000 nm, and λ= 1600 nm



Atom color: Si atoms with different local bonding, little grey sphere O.

Example 3: **Conduction fluctuations in liquid Si**



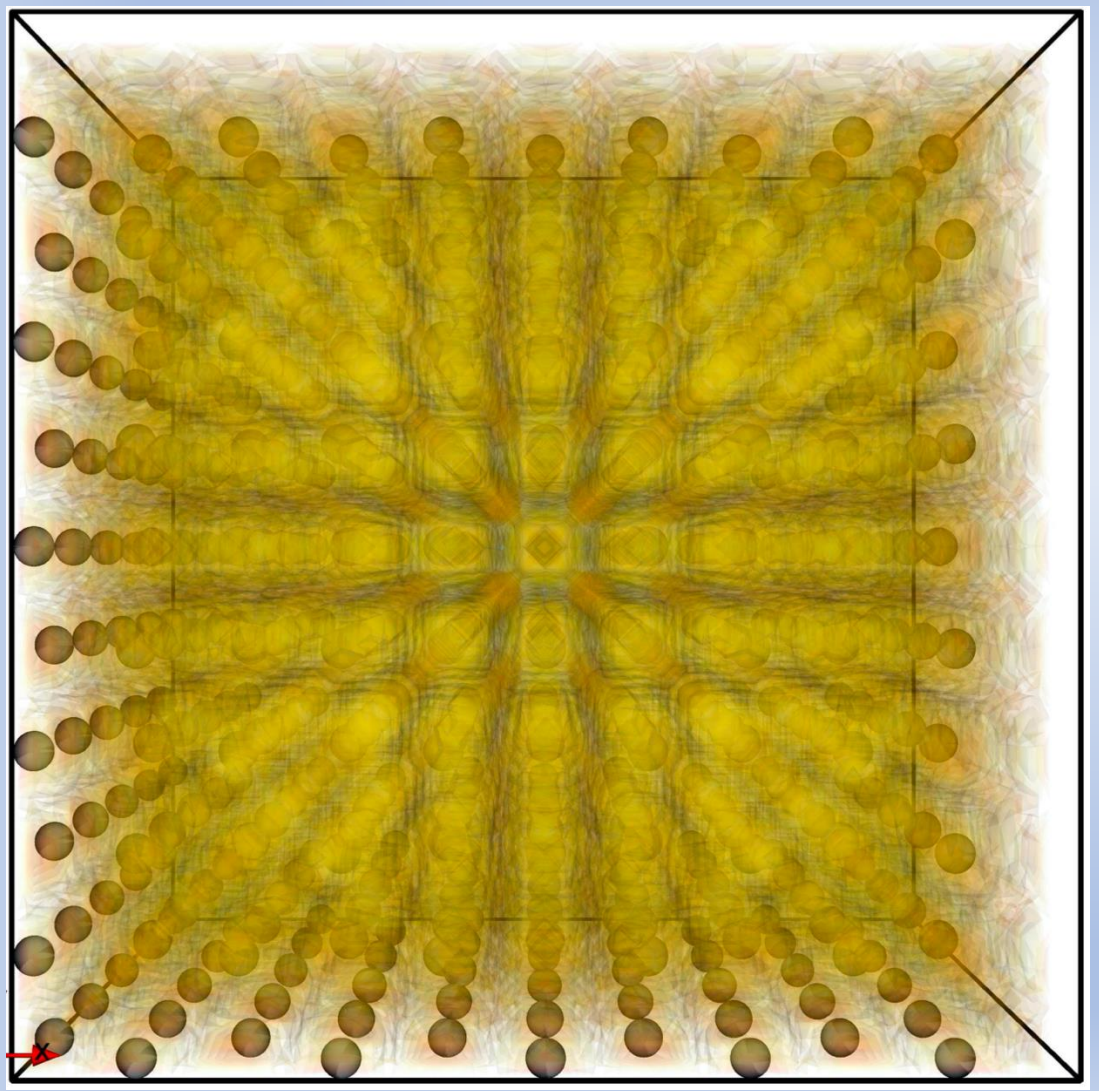
Liquid Si is a metal (mean coordination ~6, but ‘conduction centres’ moving as atoms diffuse.

Four instantaneous snapshots of SPC in liquid Si (2000K).

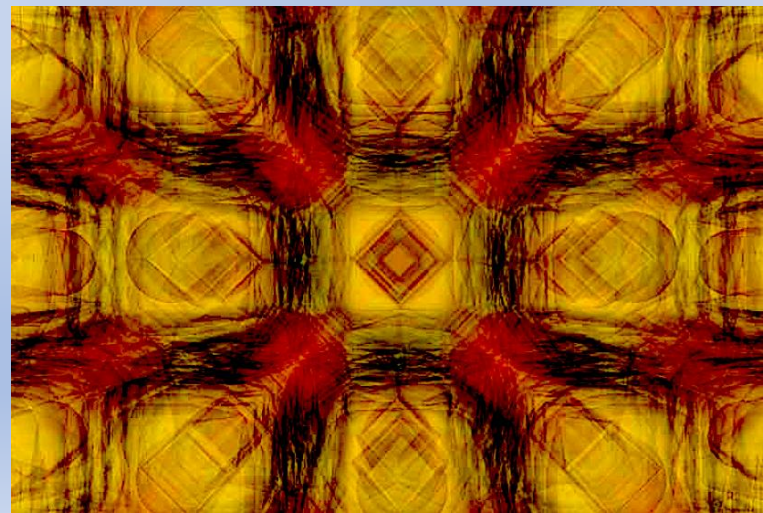
Example 4: **FCC Aluminum**

- Build a 500-atom supercell of crystalline Al
- Grid up real space on 42x42x42 grid (dim Γ=74 088)
- Compute the SPC $\zeta(\mathbf{x})$, and diagonalize Γ to obtain conduction eigenmodes.
- Illustrate the character of one such mode.

Al: Space-projected conductivity

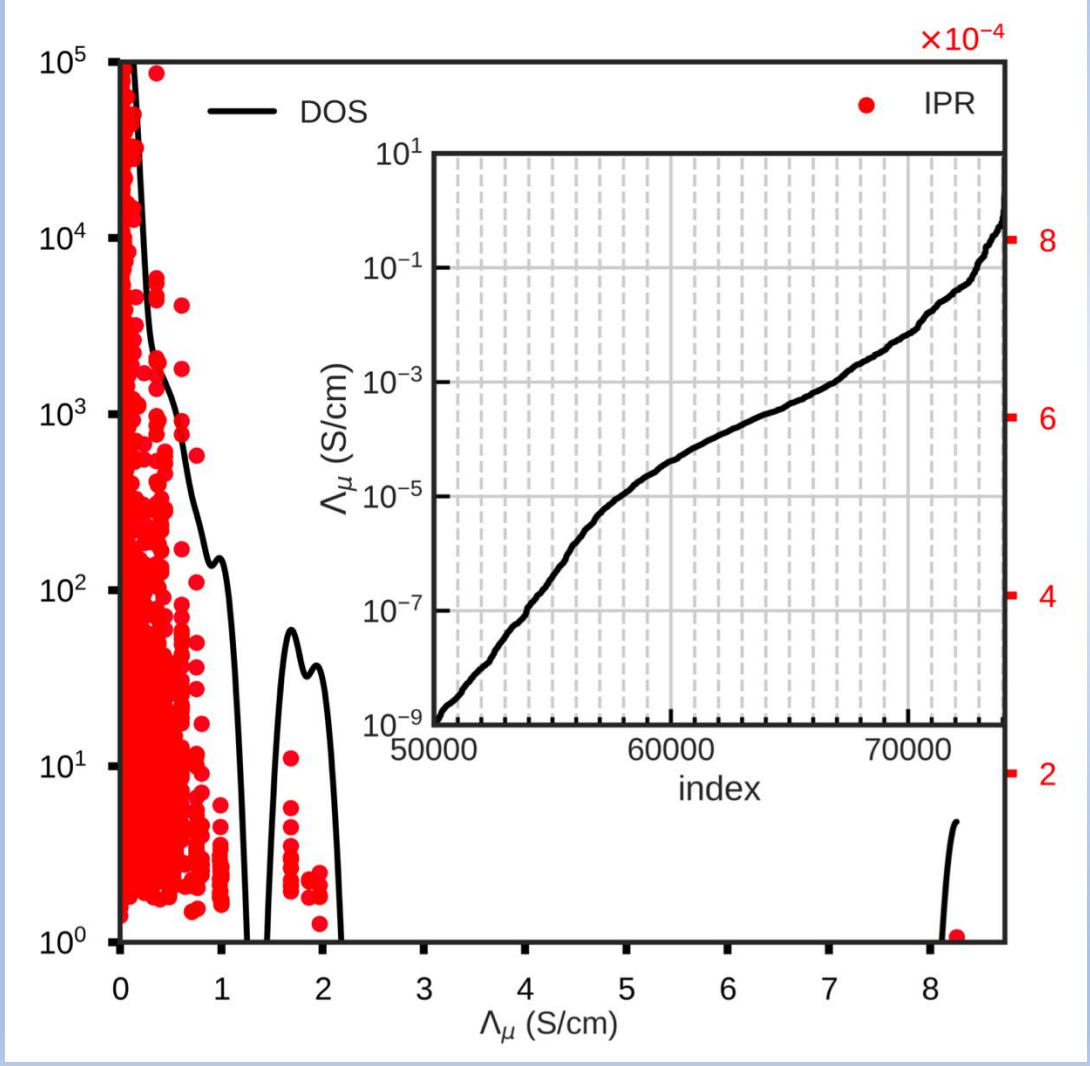


No surprise: delocalized metallic mode of conduction as we would expect.



Closeup of the centre
K. Subedi fecit.

Al: Spectral density of states for Γ



Log DOS for Γ. Note accumulation at Λ=0, even for a metal.

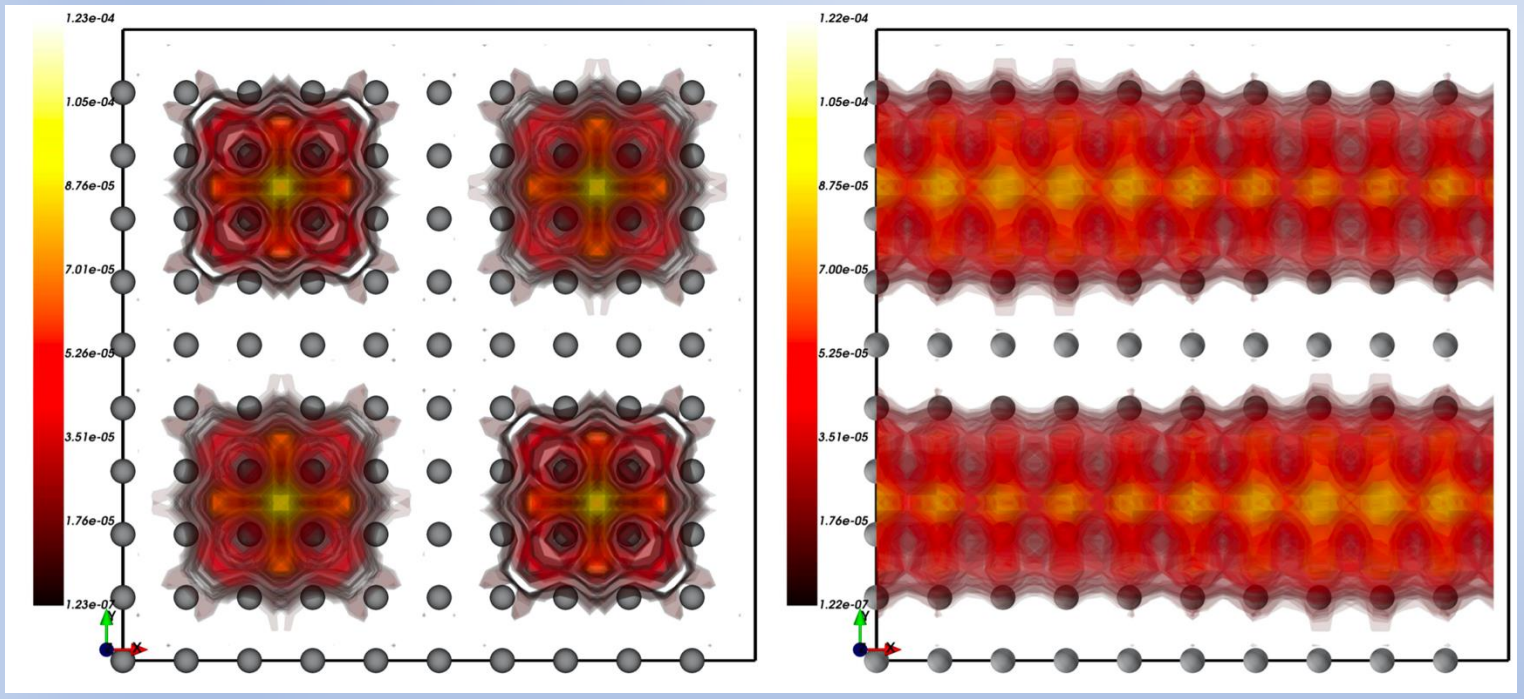
Note spectral tail for 0<Λ<1.2. Signature of metal *vs.* insulator.

Need many (~1/10) eigenvectors to get full conductivity (unlike non-metallic case).

Lots of degeneracy.

And what is that "gap" near 1.3 S/cm?

And what do these modes look like?



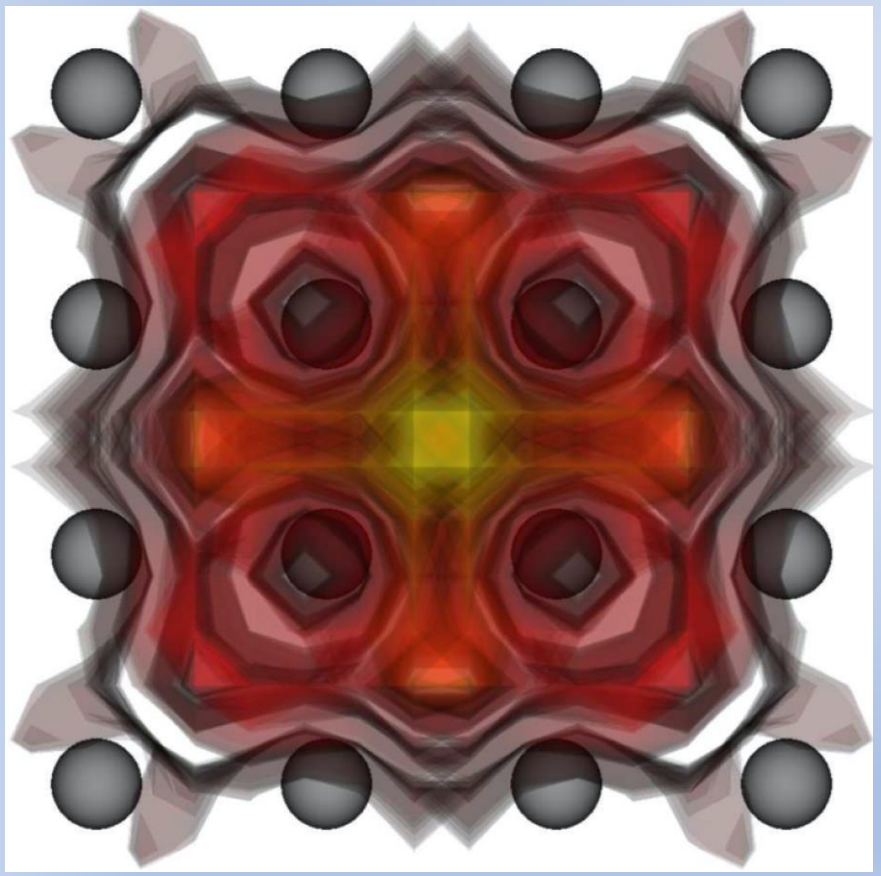
Here is one: Λ~1.0 S/cm

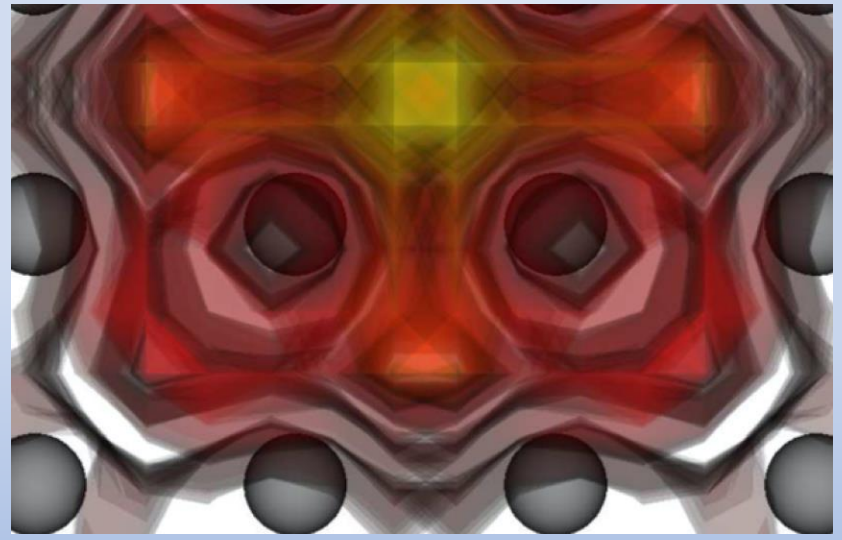
Degenerate with similar modes (in orthogonal directions)

Heat map of conduction with color coding indicated. *yellow>orange>red>black*

Hidden structure

$|\chi_\Lambda(\mathbf{x})|^2$ for Λ=1.0 S/cm

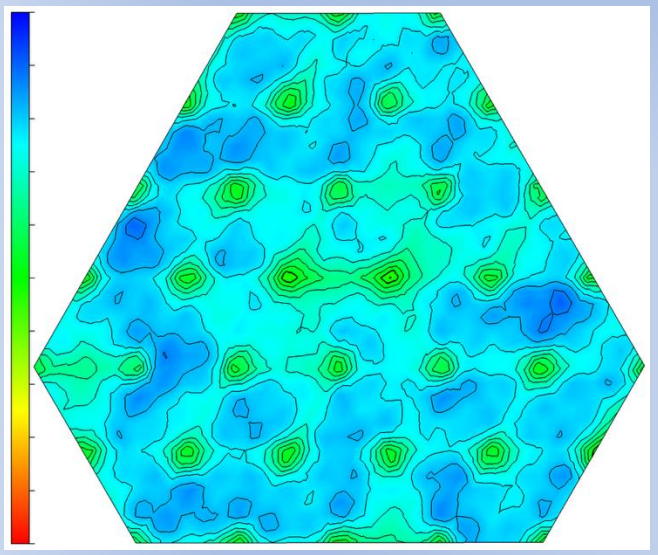


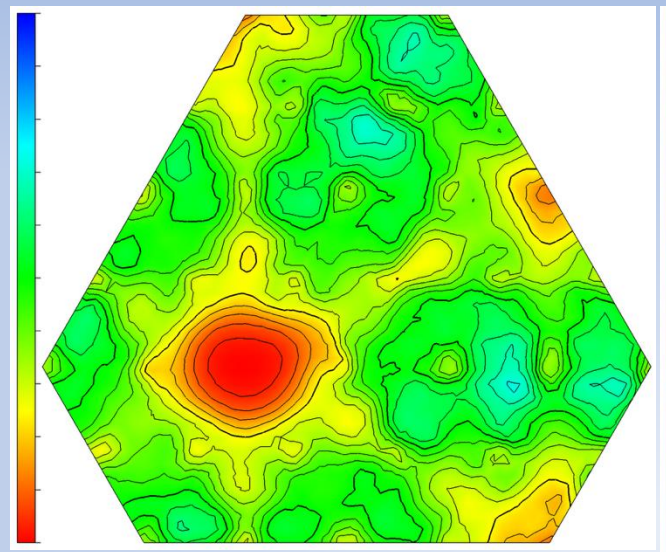


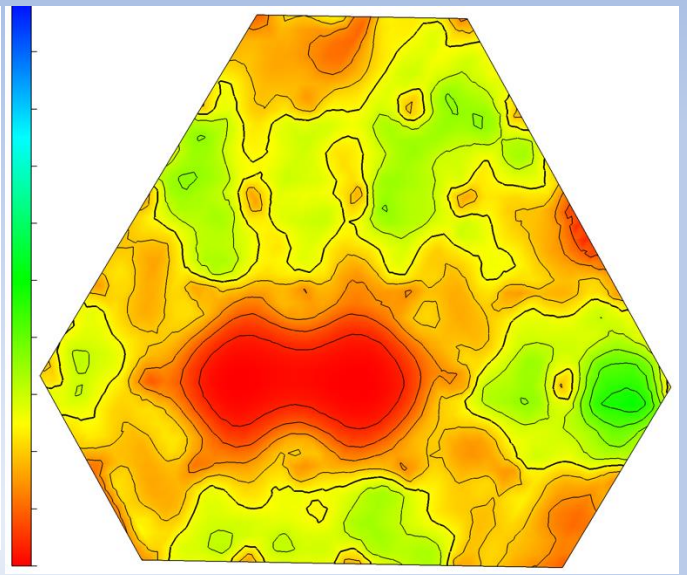
Defects in Aluminum (hot off the CPU)

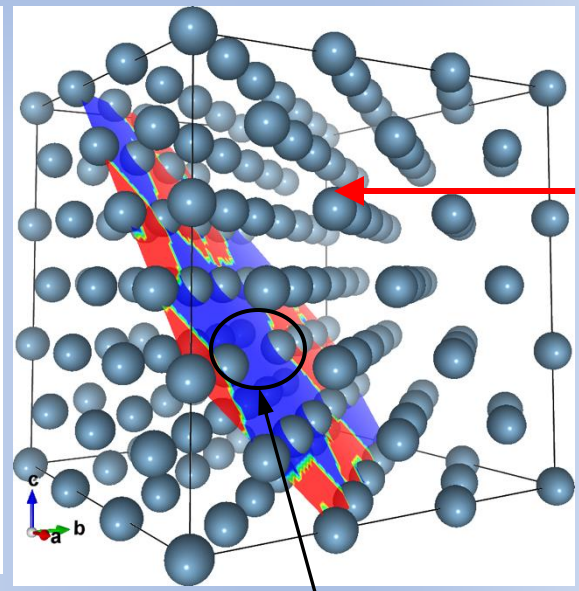
- 108 atoms (cube 12.1485 Å on an edge)
- Single- and double-vacancies were created.
- Directly compare SPC for crystal, single and di-vacancy.

SPC along 111 direction







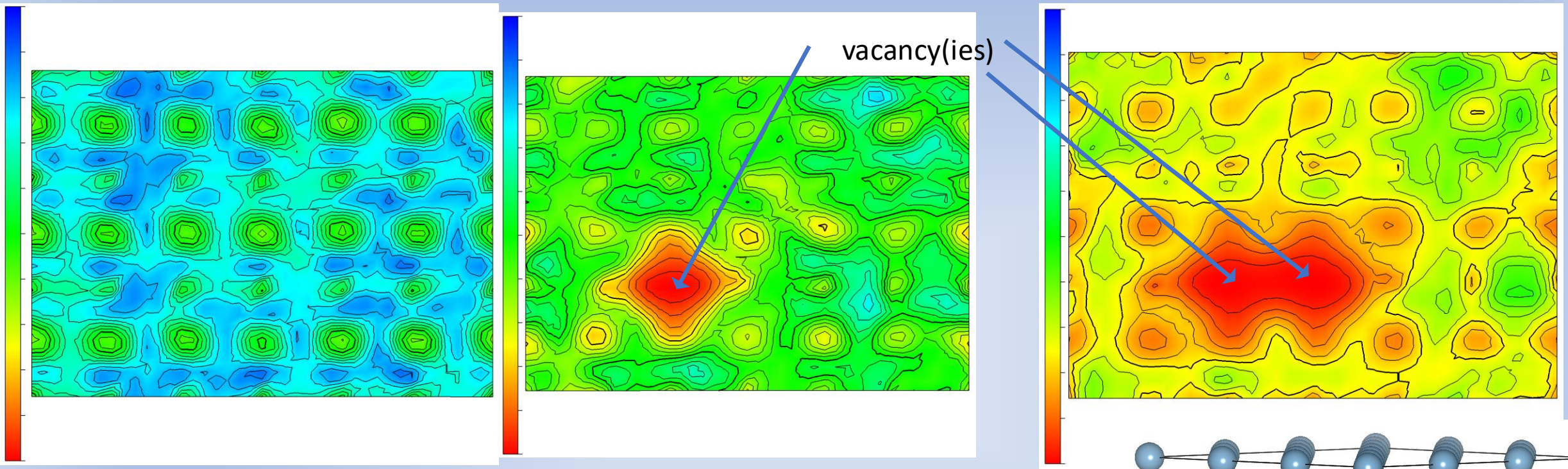


Left: crystal, middle: one vacancy and right: divacancy. The "observation direction" is shown by arrowhead.

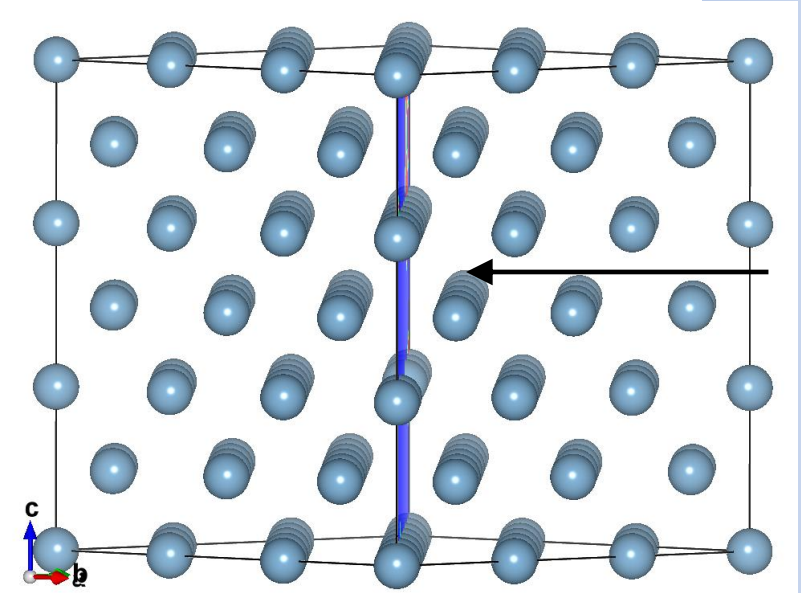
Vacancy

Colors: blue ~ 50 * red

SPC along 110 direction

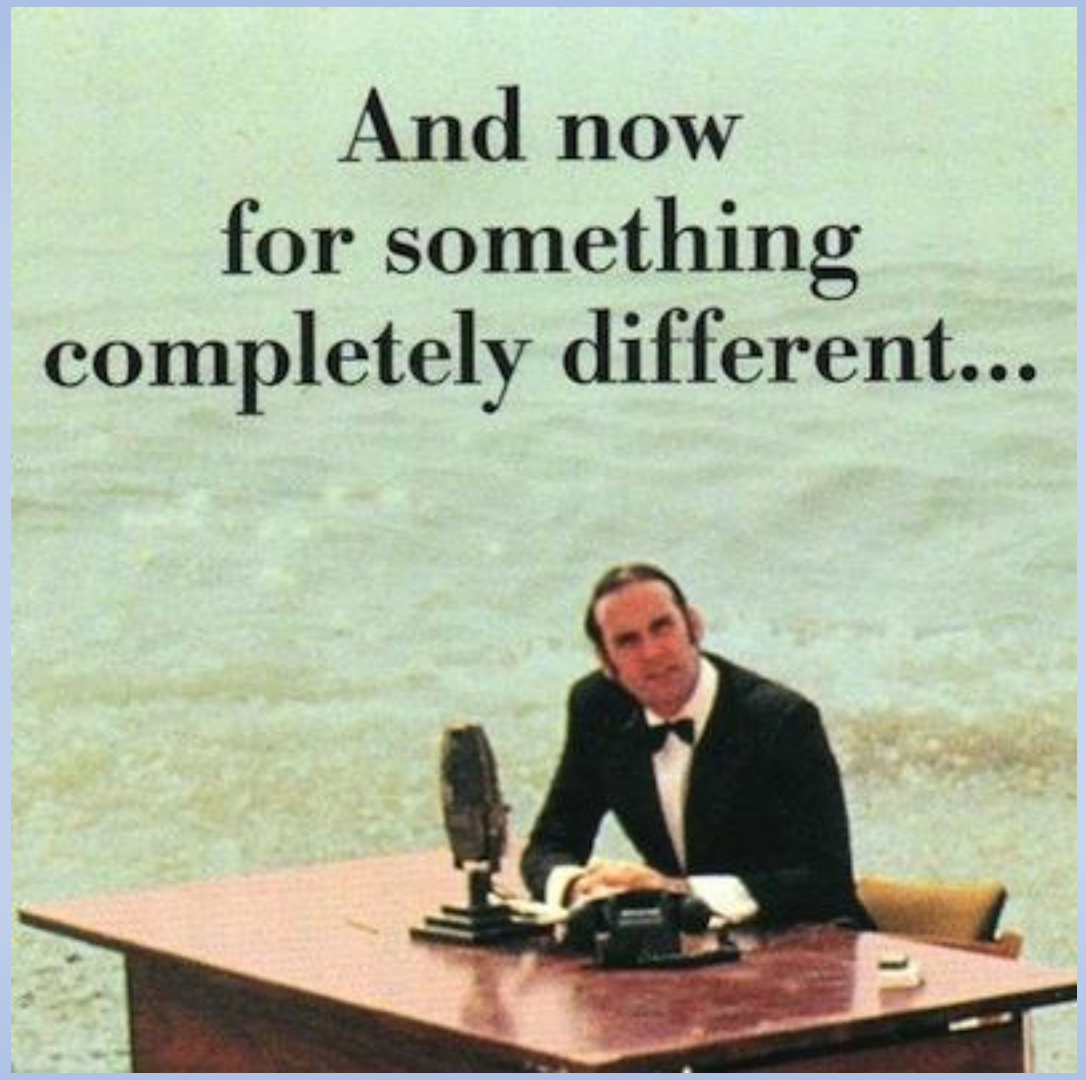


Left: crystal, middle: vacancy and right: di-vacancy



Compare conductivities

Vacancies	Conductivity (S/m)	Percentage difference	No of k-points used (4*4*4)
0	1.085E8		4
1	7.161E7	66% of no defect	4
2 (Intimate)	3.965E7	36% of no defect	12
2 (Random)	3.549E7	33% of no defect	16


And now
for something
completely different...

Aside: “Gap Sculpting”

Engineering the gap

(Key student: K. Prasai)

Idea:

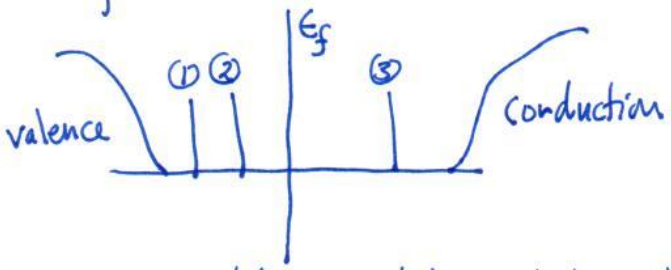
Seek a model with a specified optical gap (or lack thereof):

Try to impose *a priori* condition on gap

Motive: band gap engineering or metallization of suitable Materials (example below)

K. Prasai et al, Sci. Rept. 5, 15522 (2015); K. Prasai, P. Biswas and D. A. Drabold, 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:

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

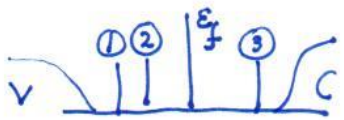
So the force is just

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

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.

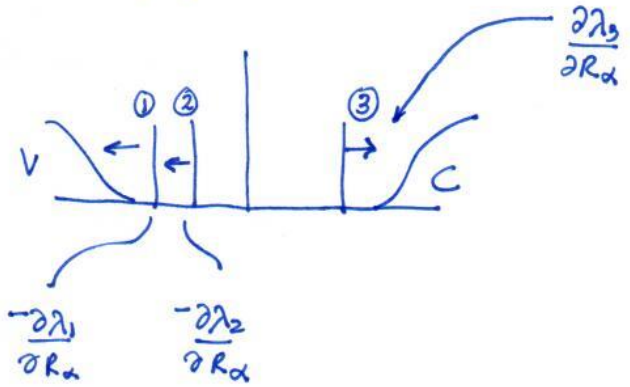
$\Rightarrow$ So to shift λ_3 toward conduction edge, move incrementally along $\underset{\sim}{e} = \partial\lambda_3/\partial R_\alpha$

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 $\mathcal{L}=\mathrm{T}-\Phi$ in which T is the usual kinetic energy, and:

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

Usual forces

$$+ \sum_i{}' \gamma g(\lambda_n) \left(\langle \Psi_n | H | \Psi_n \rangle - \varepsilon_f \right)$$

"gap clearing" (or gap cluttering) force

$g(\lambda_n)$ is picked to move valence (conduction) defect states "where we want them" (for example to open up or close a gap).

We've done it with tight binding and VASP.

Gap sculpting: continued

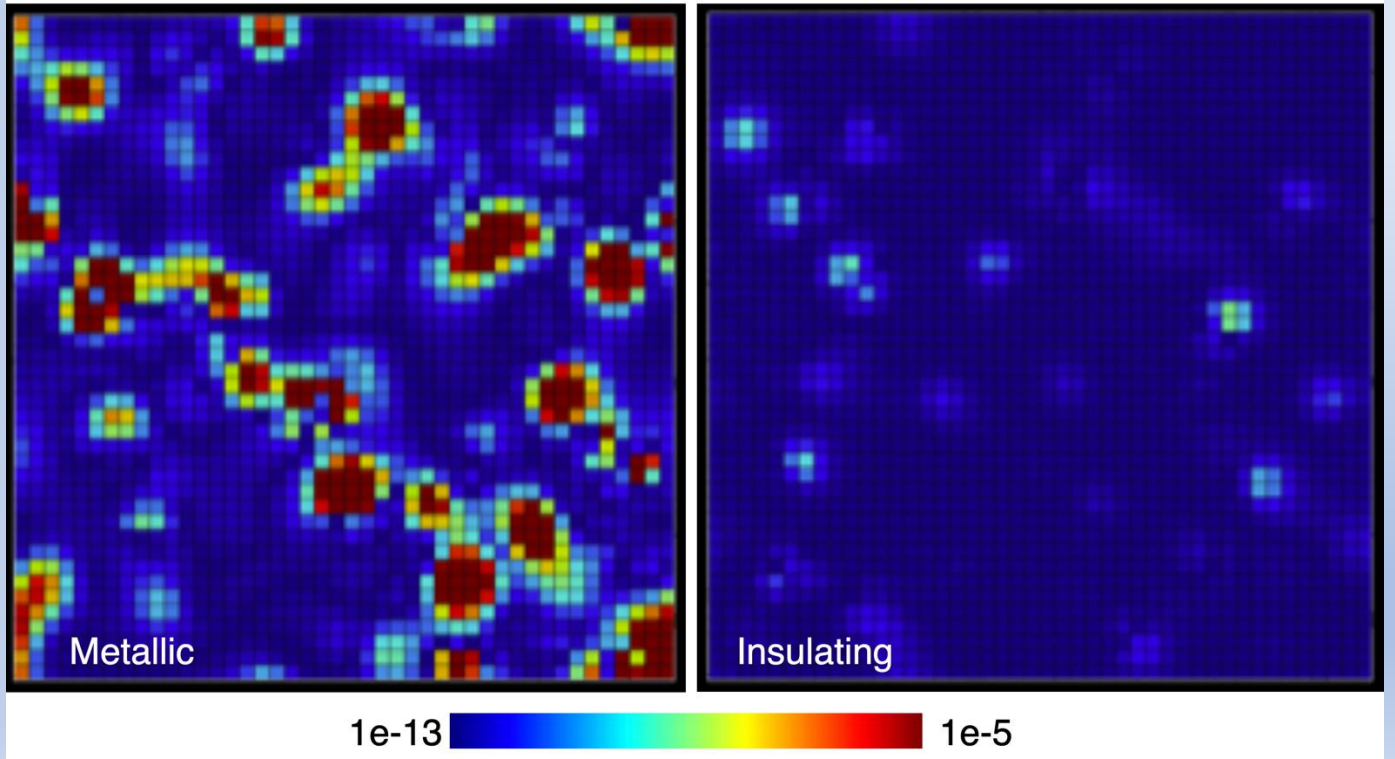
Biased dynamics (with forces added to open/close gap) at diffusive temperatures may lead to relaxed structures with engineered gap.

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 (chemistry willing) produce models with the desired optical gap.

Implemented with (VASP) and tight-binding.

Example 5: *Electronic polyamorphism* in a CBRAM material: a-$GeSe_3$:Ag

- Used "Gap Sculpting[1]" to make a conducting phase of a-$GeSe_3$ with 25% silver. *Ab initio MD* model is always semiconducting.
- "Gap Sculpting" metallized the system[2] -- $\zeta(\mathbf{x})$ heatmap:



Good conductivity *without Ag filaments*, DFT $\Delta E \sim 0.04$ eV/atom, $\sigma_m \sim 10^8\ \sigma_i$

$\sigma_m \sim 10^2/(\Omega\ \text{cm})$

Conduction through connected Ag_2Se structure.

"Electronic polyamorphism"

1. K. Prasai *et al.*, Sci. Rep. **5**, 15522 (2015).
2. K. Prasai *et al.*, P.R. Mater. **1** 015693 (2017).

Conclusions

- We describe a practical new method to obtain spatial information about charge carrier transport. It is readily implemented for any *ab initio* code.
- The matrix Γ is of significant interest: it's eigenvectors provide a compact description of transport in materials.
- Provide insight into transport in complex materials, and perhaps for applications of these (Conducting Bridge RAM, Physically Unclonable Functions…)

Bibliography

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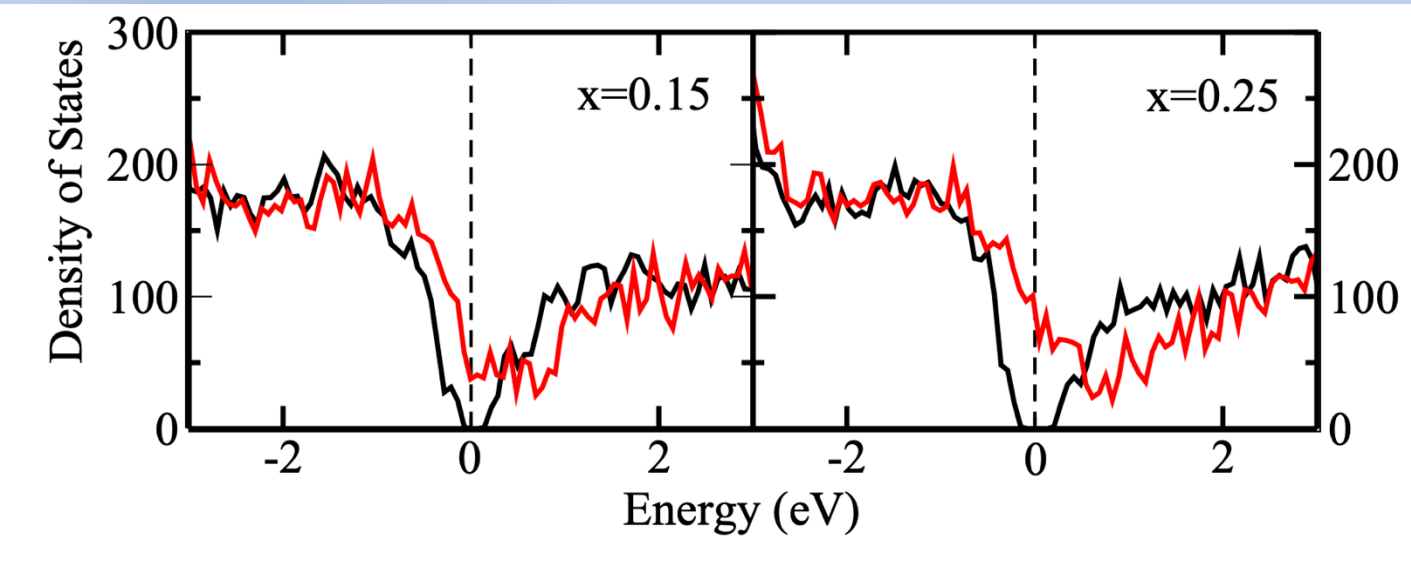
- K. Subedi, K. Prasai and DAD, *Space-projected conductivity and spectral properties of the conduction matrix*, "Form and Function of Disorder", PSSB 2000438 (2020), www.phy.ohio.edu/~drabold/pubs/238.pdf
- K. Prasai, P. Biswas, DAD "*Sculpting the band gap: a computational approach*" Sci. Rep. 5 15522 (2015); https://www.nature.com/articles/srep15522
- K. Prasai, G. Chen and D. A. Drabold, Amorphous to amorphous insulator-metal transition in GeSe:Ag glasses, Phys. Rev. Materials 1 015603 (2017)

DOS and localization of Kohn Sham states for GeSe3:Ag



K. Prasai *et al.*, P.R. Mater. **1** 015693 (2017).

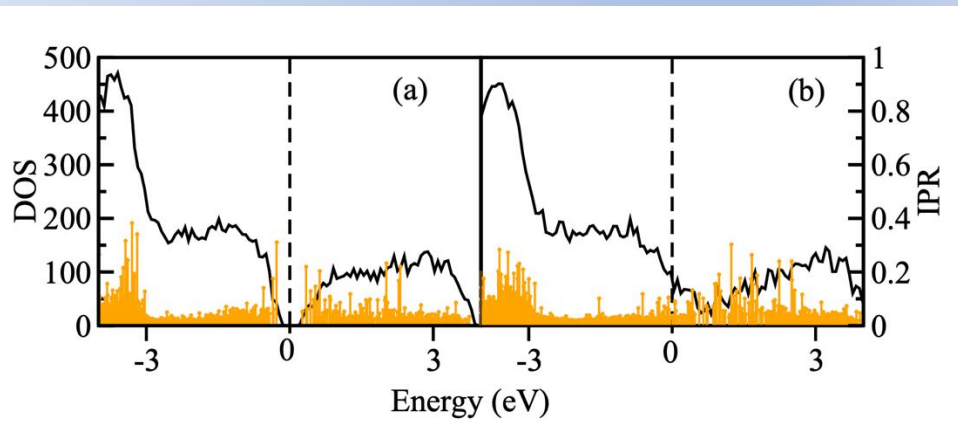


FIG. 3. The (black curve) electronic density of states (DOS) and (orange drop lines) Inverse Participation Ratio (IPR) of the insulating model (a) and the metallized model (b). The energy axis for all data sets is shifted to have Fermi level at 0 eV (highlighted by the broken vertical line).