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First Principles Modeling of Materials

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APS Tutorial

Need for first principles simulations

Observe the hard to observe:

defect wave functions
localized vibrational modes
atomistic of charge transport in molecules
magnetic moments on selected sites

Explore the hard to make:

Novel materials
Exploration of new compositions

Overcome the *plague of the macroscopic average*, obtain truly atomistic information.

Scope of the problem

- Need: Transferability of the potentials: cannot depend upon fitting to particular structures and local environments. *Prediction* depends upon this.
- Need: Efficiency to enable large models.
- Need: Broad applicability of the methods.

The formulation

- Current practical “first principles” materials theory is almost all based upon the independent electron approximation.
- These methods **fail** for strongly-correlated systems (when interactions beat the delocalization from the kinetic energy). Examples: 3d, 4d transition metals, Ce, Sm, Eu etc. *I ignore these important problems here.*

History: steps toward a practical theory

- Thomas-Fermi Models [Parr/Yang]

The electron density is a key variable to energetics

Idea: For electron gas energy E, density ρ:

E = Kinetic Energy + Exchange Energy + Hartree (Coulomb repulsion energy) + External potential:

$$A\int \rho^{5/3} dV - B\int \rho^{4/3} dV + C/2\int d^3x_1 \int d^3x_2 \rho(x_1)\rho(x_2)/|x_1 - x_2| + \int dV \rho \Phi$$

Here, A, B, C are constants, Φ is external potl. Key point: Energy is a functional of the electron density!

The purist’s starting point

To *really* get this right we need to solve

$$i\hbar \partial\psi / \partial t = H(t)\psi$$

$$\hat{H}(\{\vec{r}_i\},\{\vec{R}_\nu\},t) = \hat{T}_e + \hat{V}_{e-e} + \hat{T}_N + \hat{V}_{N-N} + \hat{V}_{e-N} + \hat{H}_{ext}$$

$$\hat{T}_e = \sum_{i=1}^{NZ_a} \frac{p_i^2}{2m}, \quad \hat{T}_N = \sum_{\nu=1}^{N} \frac{P_\nu^2}{2M}$$

… kinetic energies

$$\hat{V}_{e-e} = \frac{1}{2} \sum_{i \neq j}^{NZ_a} \frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|}, \quad \hat{V}_{N-N} = \frac{1}{2} \sum_{\nu \neq \mu}^{N} \frac{Z_a^2 e^2}{\left|\vec{R}_\nu - \vec{R}_\mu\right|}, \quad \hat{V}_{e-N} = -\sum_{i=1}^{NZ_a} \sum_{\nu=1}^{N} \frac{Z_a e^2}{\left|\vec{r}_i - \vec{R}_\nu\right|}$$

… potential energies

Not quite hopeless, but very, very hard!

Making Progress on the many-body problem

- **Born-Oppenheimer** (splitting the ionic and electronic degrees of freedom): since $m_{electron} << m_{ion}$, also can perform classical MD simulation for ions in a force field obtained from the instantaneous electronic ground state.
- Hartree, (Hartree-Fock): Use the variational principle to extract the best single-particle equations starting with product (Slater determinant) *ansatz.*
- Mathematical form of Hartree problem: "Self-consistent" Hartree equations:

$$\{-\hbar^2/2m\nabla^2 + V[\Psi_{1,2\ldots n}]\}\Psi_i = \lambda_i\Psi_i$$

Hartree and Hartree-Fock

- Still used especially in quantum chemistry community.
- Advantage: may be systematically improved “Moeller-Plessett perturbation theory” for the correlation energy “MP2, MP4”…
- Disadvantage: not very accurate in solids without heroic efforts.

Density Functional Theory

(*Kohn, Hohenberg, Sham*)

- **Theorem I**: For any system of interacting particles in external potential $V_{ext}(x)$, the potential $V_{ext}(x)$ is determined uniquely (up to a constant) by the ground state particle density $\rho(x)$.
- **Corollary**: As Hamiltonian is fully determined, so are all many-body wavefunctions. Thus **all properties** of the system are determined by $\rho(x)$.

Presentation lifted from R. M. Martin, *Electronic Structure*

DFT: II

- **Theorem II**. A universal functional for the energy E[ρ] may be defined for any external potential $V_{ext}(x)$. For given $V_{ext}(x)$, the exact ground state energy is the global minimum of this functional, and the density ρ(x) that minimizes the functional is the exact ground state density.

Tremendous advance: maps ground state energy calculation for interacting many-electron problem onto effective one-electron problem.

DFT: Get Practical

So we can write:

$$E[\rho] = \int d^3x V_{ext}(x)\rho(x) + F[\rho]$$

F is universal and unique, and E is minimized by the true ground state density, so if we knew F there would be a mathematical prescription: find the density that minimizes E and you have found the true energy and density!

but:

WHAT IS F?

What is F?

“Decompose” F into bits we expect to be there; set up so approximate part is smooth and slowly varying. We write:

$$F[\rho] = e^2/2\int d^3x_1\int d^3x_2\,\rho(x_1)\rho(x_2)/|x_1 - x_2| + T_{ni}(\rho) + E_{xc}(\rho)$$

Classical electrostatics
“Hartree” term

Kinetic energy of non-interacting electrons

What is left: exchange-correlation energy

Local Density Approximation

- We know F[ρ] and E[ρ] exactly for range of ρ for *homogeneous electron gas* from celebrated Quantum Monte Carlo calculations of Ceperley and Alder.
- So approximate:

$$E_{xc}[\rho(x)] \approx \int d^3x \rho(x) \varepsilon_{xc}[\rho(x)]$$

Idea is to “build up” the XC energy for the (weakly) inhomogeneous gas from $\varepsilon_{xc}(x)$ -- the XC energy for the homogeneous gas.

What about T_{ni}?

- If the electrons are non-interacting then:

$$T_{ni} = 2\sum_i < \chi_i | p^2/2m | \chi_i >$$

The Kohn-Sham epiphany!

Where we have the connection:

$$\rho = 2\sum_i^{n/2} |\chi_i|^2$$

Thus, if we work with $n_e/2$ orthogonal orbitals, we can get a reliable estimate for the kinetic energy.

No free lunch theorem: $n_e/2$ orbitals is a lot harder than one function ρ. Back to Hartree-like equations!

LDA is surprisingly accurate and useful

- Cohesive energies tend to be a bit high (“LDA overbinds”) typically a 10% effect.
- Can extend to spin polarized case: “Local Spin Density Approximation” (LSDA)
- For improvements in energetics, use “generalized gradient corrections”. Some of the best are somewhat empirical.

Honesty in advertising

- While DFT in the LDA can be excellent for energies and forces, it *does not directly yield the correct optical gap.* After all it is a **ground state theory!**
- Of course there are fundamental limitations to the independent-particle picture, so *don't expect good results for highly correlated systems.*

Math/computation: The Kohn-Sham equations

$$\{-\hbar^2/2m\nabla^2 + V_{ext}(x) + V_{Hartree}(x) + V_{xc}(x)\}\chi = \lambda\chi$$

Note: really the Hartree and XC terms depend on ρ, and thus These equations are non-linear and must be iterated to "self-consistency".

The fundamental equation of practical density functional theory

Pragmatism

- Pseudopotentials: enable accurate calculations only (explicitly) handling the valence electrons (4 for Si, not 14!)

  key ideas: Herring, Phillips, Hamann, Vanderbilt

- As this is quantum mechanics, practical calculations require a choice of *representation.*

Name your poison: plane waves or local orbitals

$$|\chi> = \sum_{G\neq 0} a_G |G>$$

PLANE WAVE BASIS

G are reciprocal lattice vectors, |**G**>, plane waves

Car-Parrinello, Payne
VASP, CPMD, ABINIT
FHI98MD, (others)

$$|\chi> = \sum_{\mu} a_\mu |\mu>$$

LOCAL BASIS

μ is local basis function, usually atomic-like orbitals, blips *etc*.

Sankey *et al FIREBALL*
Ordejon *et al SIESTA*
(others)

Excellent implementations of both available

“Order N” Methods

- The CPU demand scales at least like N^3 for N the number of electrons. Often want models with 10^2-10^4 atoms. *Big problem!*
- In systems with an optical gap, can work with “generalized” Wannier functions (localized in real space) or a truncated density matrix. With real-space localized representations, linear scaling “O(N)” is possible. (Vanderbilt, Mauri *et al*, Ordejon *et al*, many others)
- All bets are off for O(N) for metals!
- This is a research area, not a black box area!

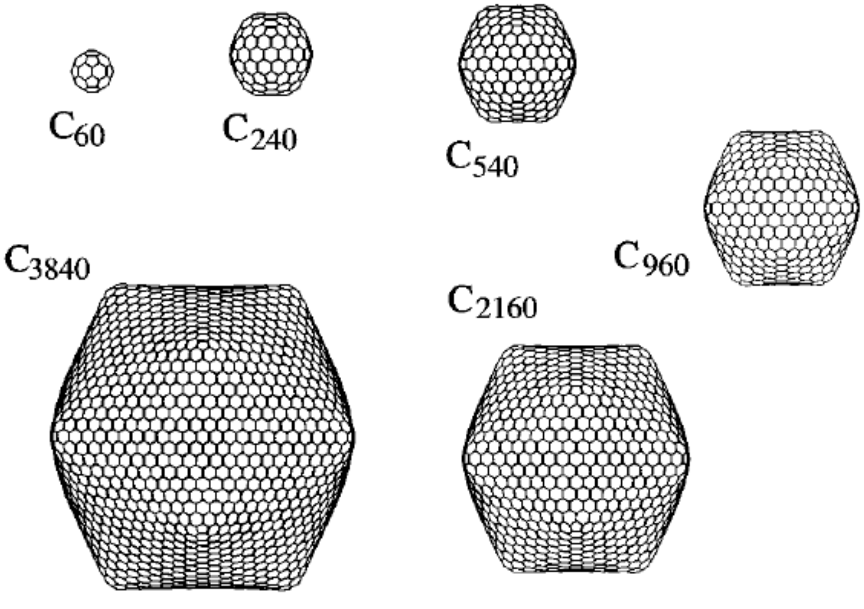
Personal biases before applications

- ***Use the method that makes the most sense.***
- Ex: DNA -- do it with local basis methods (require order N and its not really periodic)
- Ex: Periodic systems and high precision, use plane waves.
- Bells and whistles already implemented might well play a role. These are usually huge and complex codes you will not want to write yourself.
- **Of course** empirical potentials or tight-binding may be the right choice for very large systems or qualitative accuracy!
- Finally, remember that all this is approximate. Often extraordinarily reliable, but care is still needed!

First some fun. Cluster to nano to crystal.*Simple O(N)*

- How do discrete electronic and vibrational molecular levels form bands? *Note the faceted, flat, locally "graphitic" faces.*
- We directly compute this for icosahedral carbon fullerenes with 60-3840 atoms and compare to an exact (k-space) calculation for monolayer graphite.

We use a tight-binding Hamiltonian here.



Sample calculation: **estimating the density of states of any big matrix**

- Strategy: convert the computation of the density of states (DOS) into the classical (Hausdorff) moment problem.
- Solve the moment problem with information theory (the method of maximum entropy).

Computing density of states "order N"
A Moment approach PRL $\underline{70}$ 5631 '93

1) Let H be large, sparse, symmetric matrix.

$$\dim(H) = m$$

2) Let $|x\rangle$ be a m-vector.

3) Let $\nu_n(|x\rangle) = \langle x| H^n |x\rangle$

$$= \sum_{ij=1}^{m} x_i x_j \; (H^n)_{ij}$$

↖ $j^{\underline{th}}$ comp. of $|x\rangle$.

4) Consider an ensemble average over $|x\rangle$:

$$\overline{\nu_n(|x\rangle)} = \sum_{ij=1}^{m} \overline{x_i x_j} \; (H^n)_{ij}$$

Select the ensemble $\{|x\rangle\} \ni \overline{x_i x_j} \rightarrow \delta_{ij}$

(easy: select components of $|x\rangle$ independently from unit normal distribution)

THEN: $\overline{\nu_n(x)} \rightarrow \sum_{ij=1}^{m} \delta_{ij} (H^n)_{ij} = \sum_i (H^n)_{ii} = \mathrm{Tr}(H^n)$

Note: $\mu_n = \int_{-\infty}^{\infty} dx\, x^n \underset{\uparrow \text{DOS}}{\rho(x)} = \mathrm{Tr}(H^n)$

5) For integrated quantities ($\epsilon_F, \epsilon_{BS} \cdots$) use special vectors which match $n=0,1,2$ moments : Select $|x^*\rangle \ni$

(i) $\langle x^*|x^*\rangle = 1$ (normalization)

(ii) $\langle x^*|H|x^*\rangle = Tr(H)$

(iii) $\langle x^*|H^2|x^*\rangle = Tr(H^2)$

Can compute $O(N)$

[$|x^*\rangle$ obtained by minimizing

$$0 = \pi(x^*) = \left[\langle x^*|x^*\rangle - 1\right]^2 + \left[\langle x^*|H|x^*\rangle - Tr(H)\right]^2 + \left[\langle x^*|H^2|x^*\rangle - Tr(H^2)\right]^2 .$$

6) Use "maximum entropy" methods to solve the classical moment problem :

Given:

$$\overline{\nu_n} = \int_{-\infty}^{\infty} dx\, x^n \rho(x) \quad n = 0,1,2 \cdots N < \infty$$

Whats an optimal guess for ρ?

WARMUP: Aside; solving the maxent moment problem

Suppose all we know is $\mu_n = \int_a^b dx\, x^n \rho(x)$ $n = 0, 1, \cdots N < \infty$

$\rho(x) \geq 0$

How do we use maxent to compute a guess for $\rho(x)$?

Maximize: $- \int_a^b dx\, \rho(x) \ln \rho(x)$

uniform measure

subject to $\mu_n = \int_a^b dx\, \rho(x) x^n$

Mead & Papanicolaou, 84
Biswas, 05

Construct

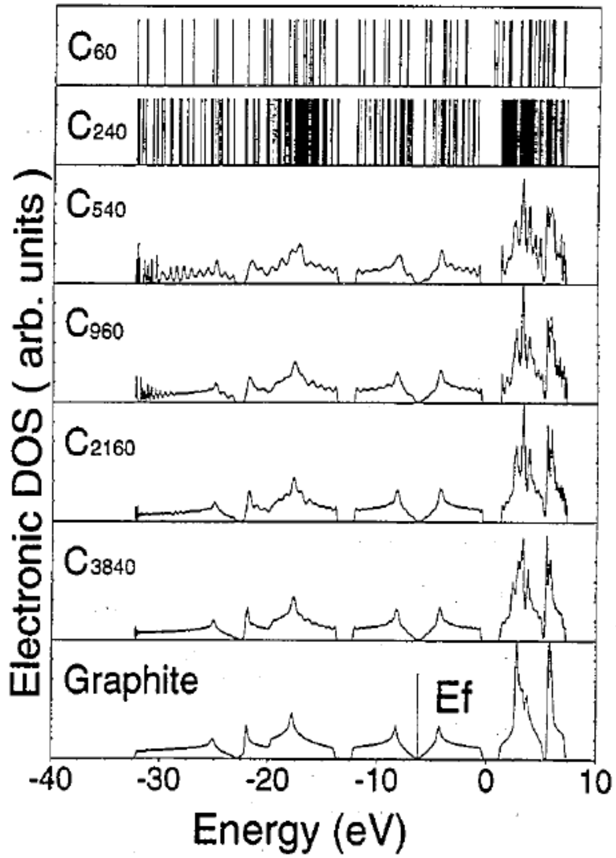
$$\mathcal{H}^* = - \int_a^b dx\, \rho(x) \ln \rho(x) + \sum_{i=0}^{N} \lambda_i \left[\int_a^b dx\, \rho(x) x^i - \mu_i \right]$$

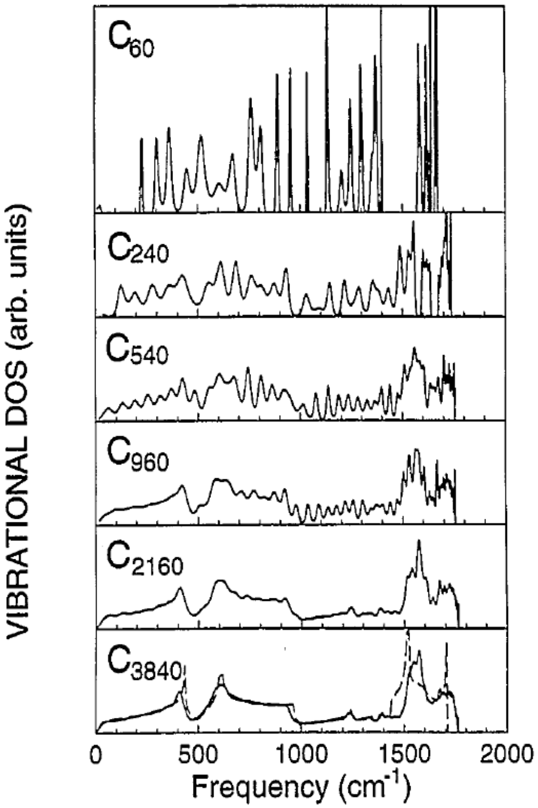
$$\frac{\delta \mathcal{H}^*}{\delta \rho} = 0 \Rightarrow \rho(x) = \text{const} \times \exp\left\{ - \sum_{i=1}^{N} \lambda_i x^i \right\}$$

and $\{\lambda_i\}$ are determined by moment conditions.

Note – for numerical convenience use orthogonal polynomials, not raw powers!

Cluster to crystal: electrons and phonons





SSC **96** 833 (1995), PRL **75** 1324 (1995) Ordejon, Martin, Dong, DD.

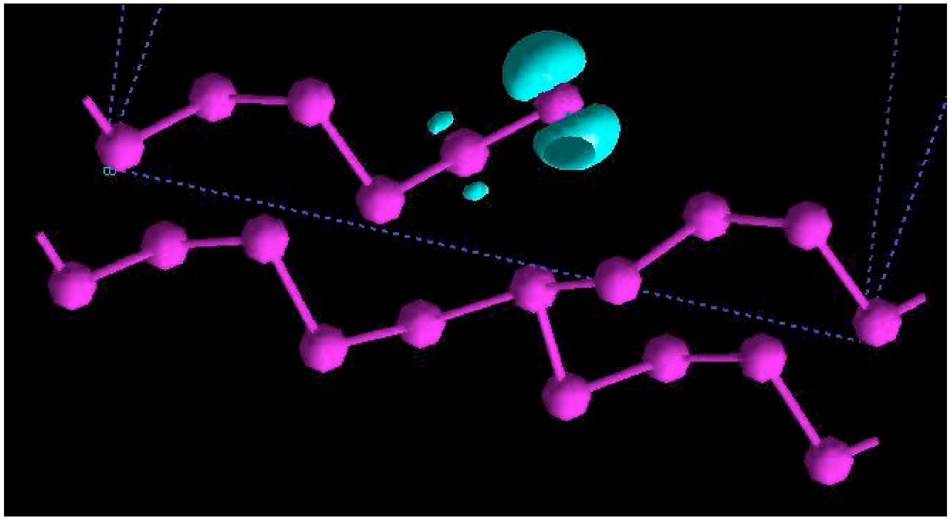
A few brief comments

- Can observe the formation of bands; directly track the molecular to solid transition.
- Van Hove singularities at some band edges
- Emphasizes that the electronic (and vibrational) structure depends upon the local environment.

DFT: Examples

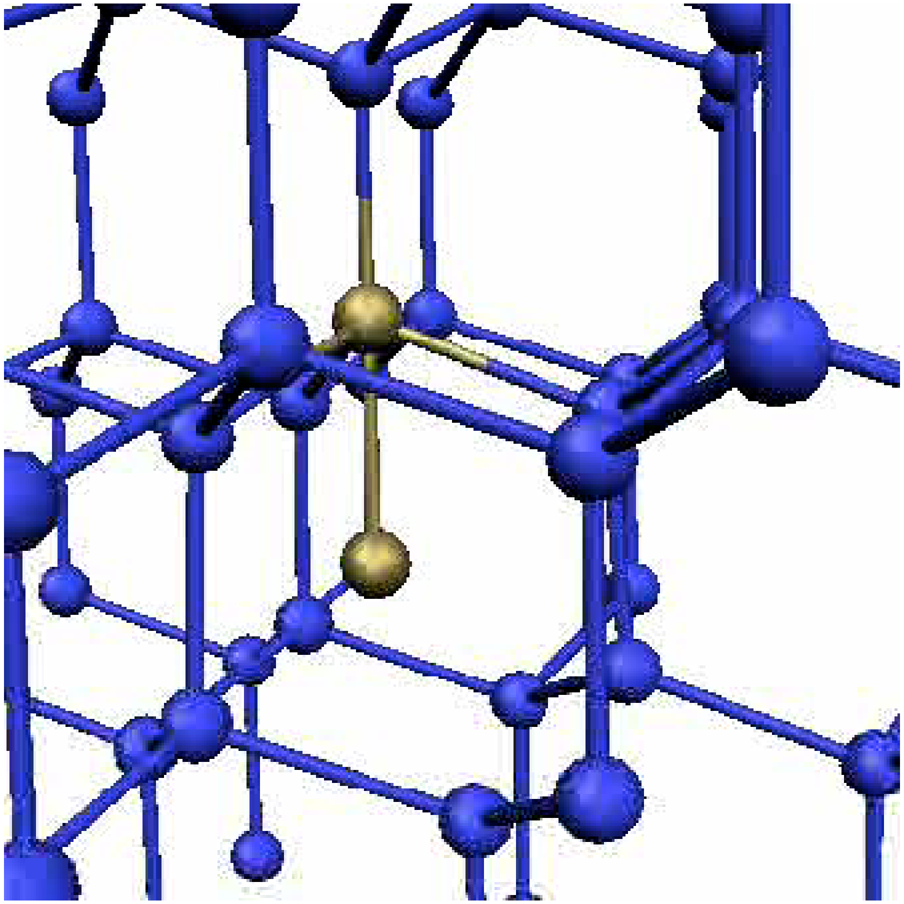
- Portrait of a famous defect
- Cu pair in Si: The Movie
- Si(111) 7x7 surface
- Biomolecules
- Magnetic properties
- Glasses

Valence alternation pair defect in Se



With X. Zhang, using SIESTA and CASTEP. The unpaired electron spin density is turquoise near the chain end.

Vibrational mode of Cu dimer in Si



Thank you **Stefan Estreicher**, Tx. Tech.
PRL **90** 035504 (2003).

substitutional-interstitial copper pair local mode

Si(111) 7x7 reconstruction

Brommer *et al* PRL ‘92

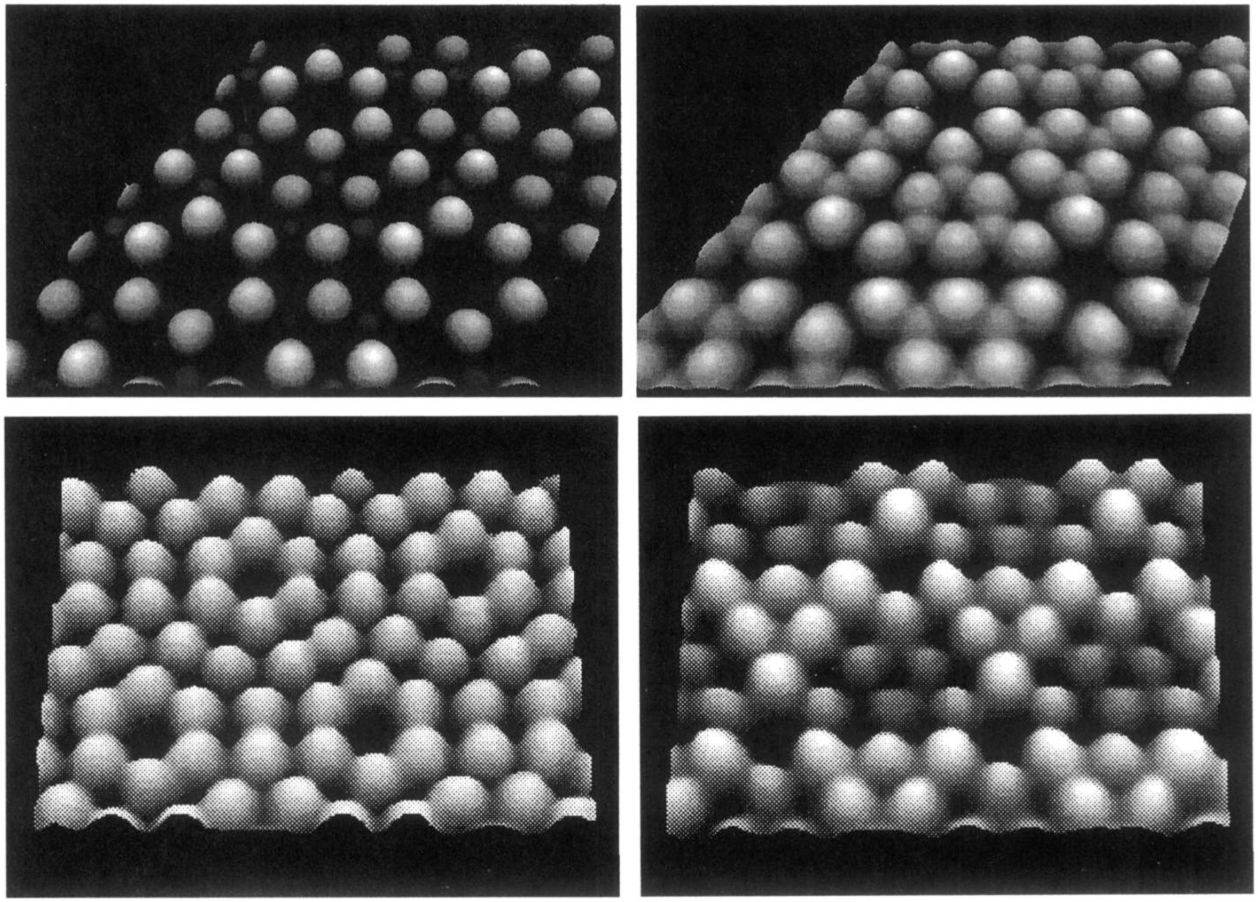


FIG. 2. STM images of the Si(111)-(7×7) surface reconstruction based on the results of this calculation (top panels), and the experimental results of Avouris and Wolkow [17] (bottom panels). Shown are unoccupied (left panel) and occupied (right panel) state contributions. The determination of the grey scale in the top panels is described in the text.

Si(111) 7x7

- Old (1992) but still impressive calculation of 111 reconstruction on ~700 atom slab.
- Find that 7x7 reconstruction is favored over expected 2x1 by about 60 meV/cell.

DNA: under the mathematical microscope

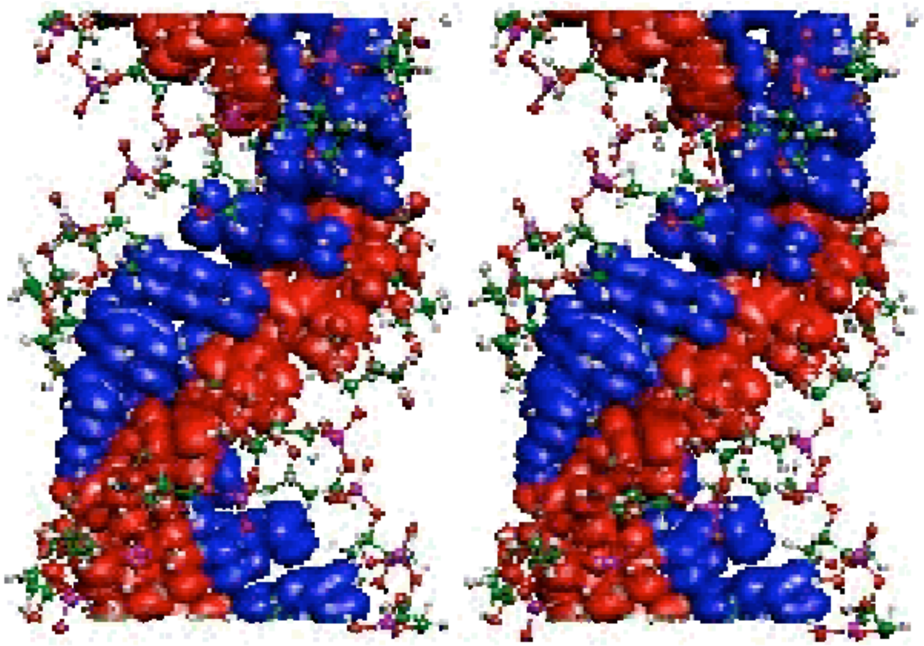
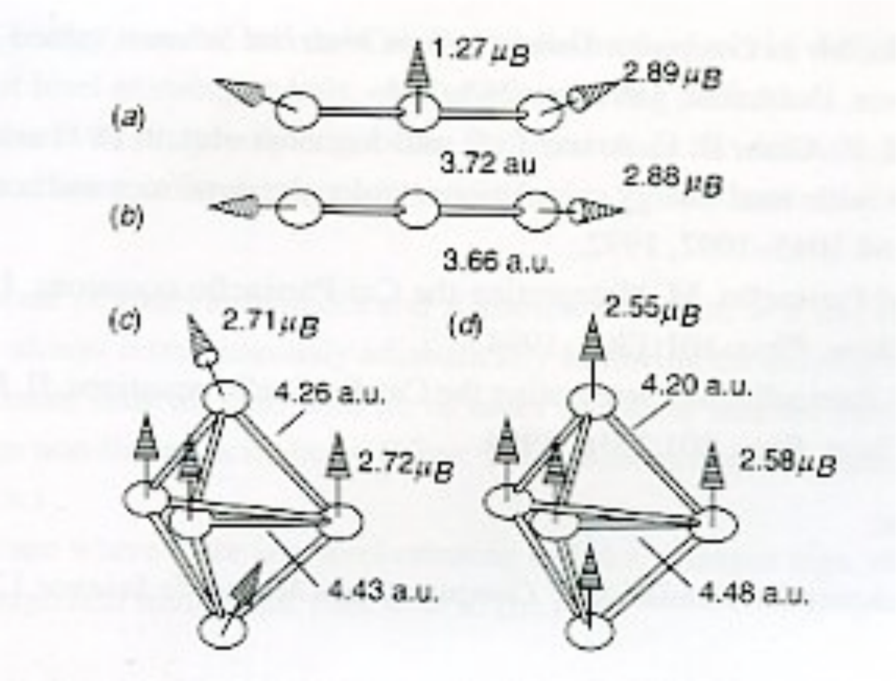


FIG. 2: (Color stereogram) Surfaces of constant density (1.5 10^5 $e^-/\text{Å}^3$) for the states corresponding to the lowest unoccupied band (red), and highest occupied band (blue) of the ordered pGpC structure. The graphs were produced with Molekel [64].

There is wide interest in DNA as a conductor. This is a simulation showing those states which could be involved in conduction. ~1000 atoms. Local basis order N approach used.

Artacho *et al* *SIESTA*

Structure and moments of Fe clusters



T. Oda *et al.* PRL ‘98
Car-Parrinello CPMD

Fe atoms and the moment at each site

Glasses

Basic problem: *Where are the atoms?!* Here I discuss:

- Computer “glass making” and the motion of Ag ions in glassy chalcogenide hosts.
- Complex pressure-induced phase transition in amorphous silicon.
- For more on better ways to make model glasses come to my talk tomorrow.

Modeling glasses and amorphous materials

Glasses are interesting and challenging

1) To sensibly model with periodic BC need large models -- at least a few atom atoms.
2) Hard to really simulate glass formation -- simulation time scales are far too short.
3) They are ubiquitous (windows, wine glasses, TFTs for laptops, solar cells, DVD media)
4) They are interesting (Anderson transition *etc*.)

Glass a’la Computer

1. Build a cell (with ~ 200 atoms) and periodic boundary conditions with the atoms you want.
2. Cook/anneal -- form an equilibrated liquid a bit above T_m.
3. Simulate quenching it -- remove kinetic energy “dissipative dynamics” until motion is arrested. This is the model of the glass!

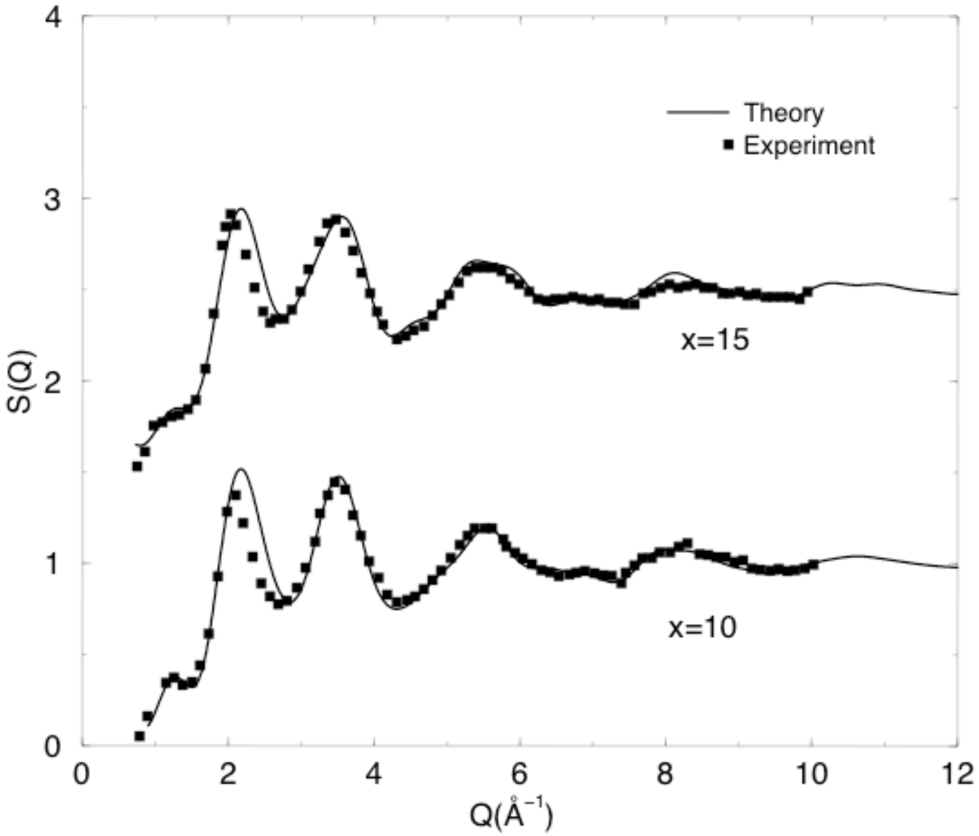
Melt quench example: silver ion dynamics in Ge_xSe_{1-x}:Ag

- An important problem: *How does Ag diffuse in chalcogenide hosts?* **Silver is incredibly mobile in GeSe glasses.**
- Key to understanding/optimizing Programmable Metallization Cell (memory device), photo-response of Ag etc
- Fundamental problem in solid state ionics

Approach

- Use Fireball2000 (J. Lewis *et al*. local basis *ab initio*) MD
- Cook and quench in conventional way, forming models of a-$(GeSe_3)_{.9}Se_{.1}$:Ag and a-$(GeSe_3)_{.85}Se_{.15}$:Ag *(10-15% Ag in models)*
- Study the Ag dynamics directly from thermal MD simulation.

GeSe:Ag Models (240 atoms)

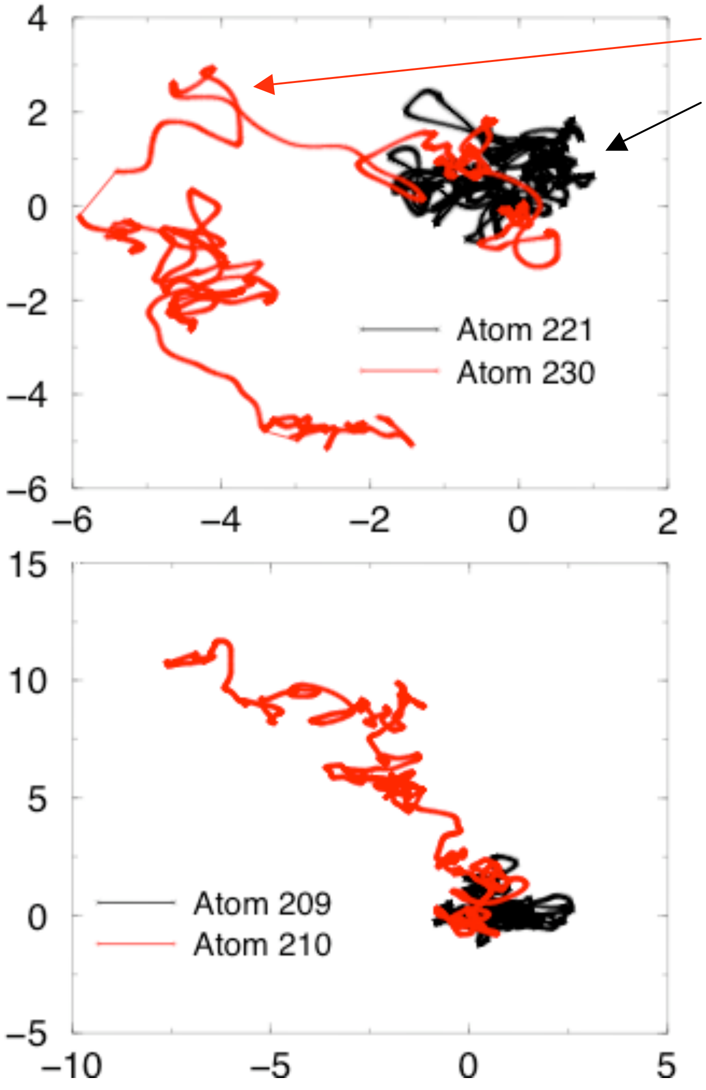


Static structure factors.

Experiment:
A. Piarristeguy, J. Non-Cryst. Sol. **332**, 1 (2003).

Ag$^+$ hopping from thermal MD

Thermal MD, constant T, 20 ps, *ab initio* Interactions.



Most diffusive Ag atom

Least diffusive Ag atom

Dance of the silver atoms

Some first inferences

- There are *trapping defects.* This is a *direct observation* of the proposed Scher-Lax-Phillips[1] traps. Trap model is very successful with relaxation data.
- There is free volume (reduced local density) for rapid diffusers.
- We need statistics! Absorption and emission rates of cages, temperature dependence etc. All in progress.
- Some goals: provide the microscopic parameters for the trapping model, elucidate the microscopic (and dynamic) nature of the traps.

[1] J. C. Phillips, Rep. Prog. Phys **59** 1133 (1996).

A prediction: amorphous GaN

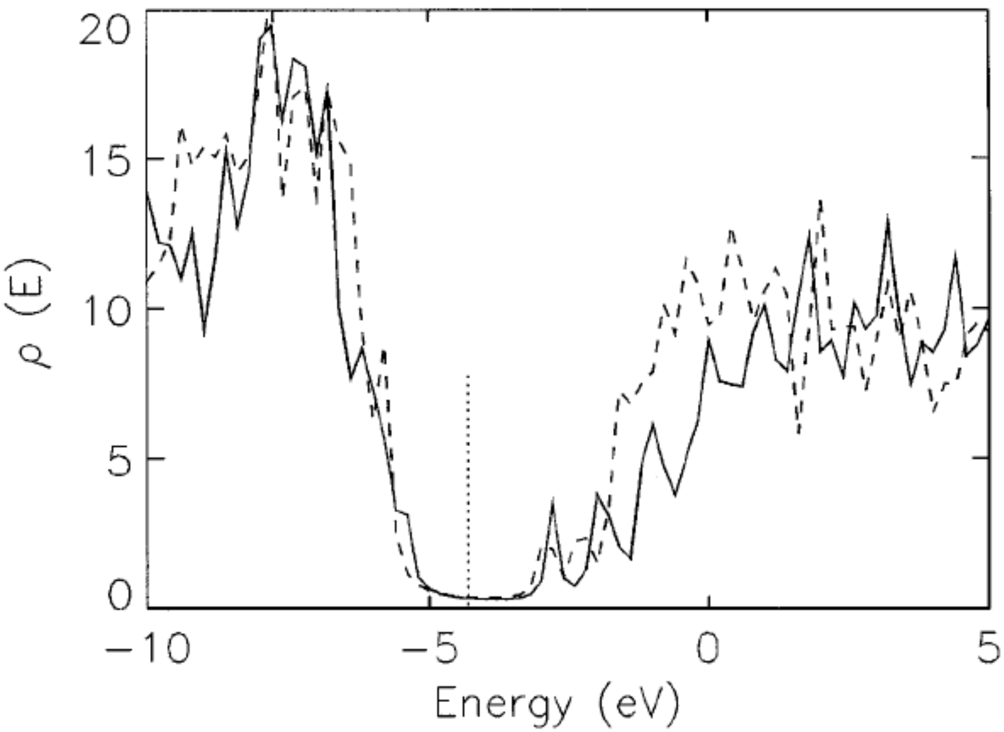


FIG. 2. Electronic density of states. The vertical dashed line is the Fermi level. We can roughly predict an experimental gap of 2.8 eV for both models, surprisingly independent of the threefold content. The broadening used was 0.1 eV.

Stumm & DD PRL **79** 677 ‘97

We show that an amorphous phase of GaN can have a state free gap.

Since grown by Kordesch, Silva, Others.

APL **77** 1117 (2000).

Pressure-induced phase transition in a-Si

Ingredients:

- Constant pressure MD simulation, Sankey Hamiltonian (local basis LDA).
- 216 atom models of a-Si from Mike Thorpe (ASU): highly realistic models of a-Si.

Approach:

- Simulate applied pressure and track the structural response

Response to pressure: first order transition?

AB INITIO SIMULATIONS OF FIRST-ORDER . . .

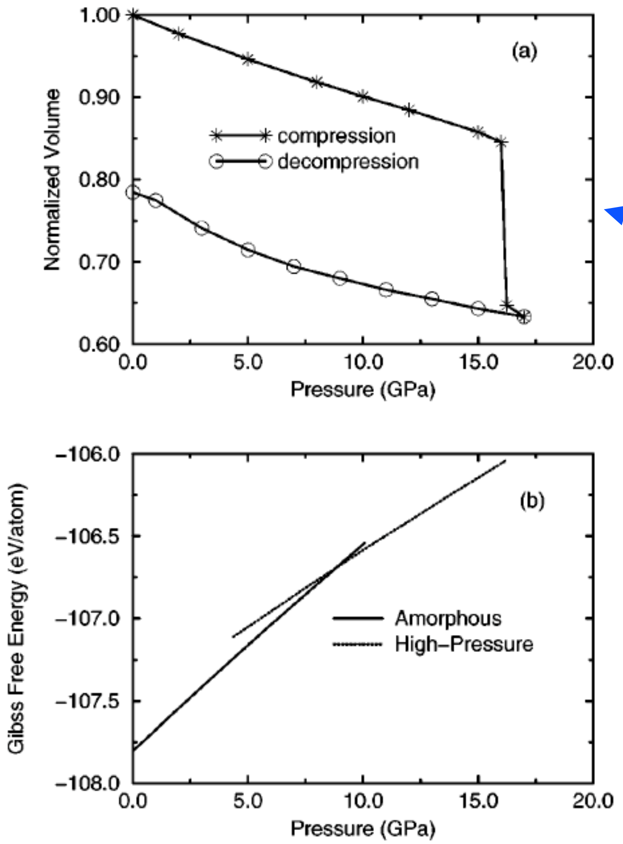
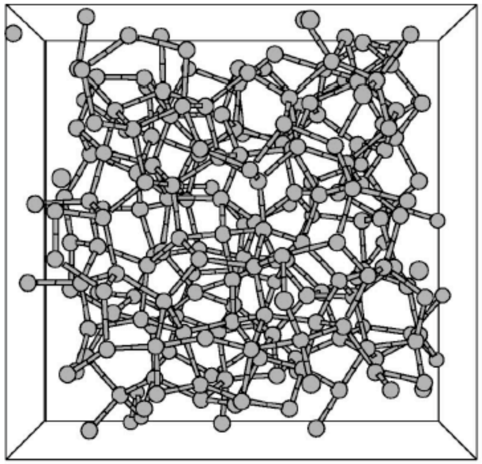


FIG. 1. (a) The normalized volume of *a*-Si to the zero-pressure measured volume. At 16.25 GPa, the volume drops suddenly, indicating pressure-induced phase transition. (b) Gibbs free energy of amorphous and high pressure phase cross near 9 GPa implying a transition.

Volume vs. Pressure

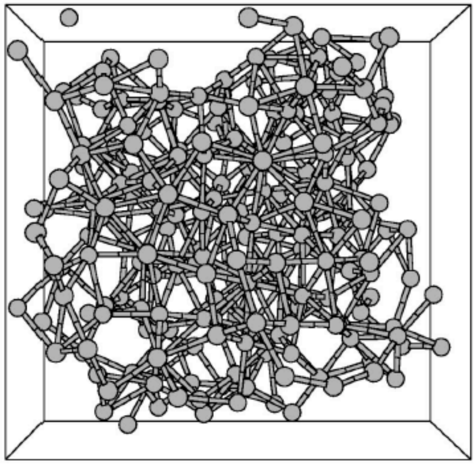
abrupt collapse

a-Si, P=0



(a)

High pressure metallic phase 16 GPa



(b)

Durandurdu, DD PRB **64** 2001

Electronic Structure and Pressure.

How the Insulator-metal transition occurs

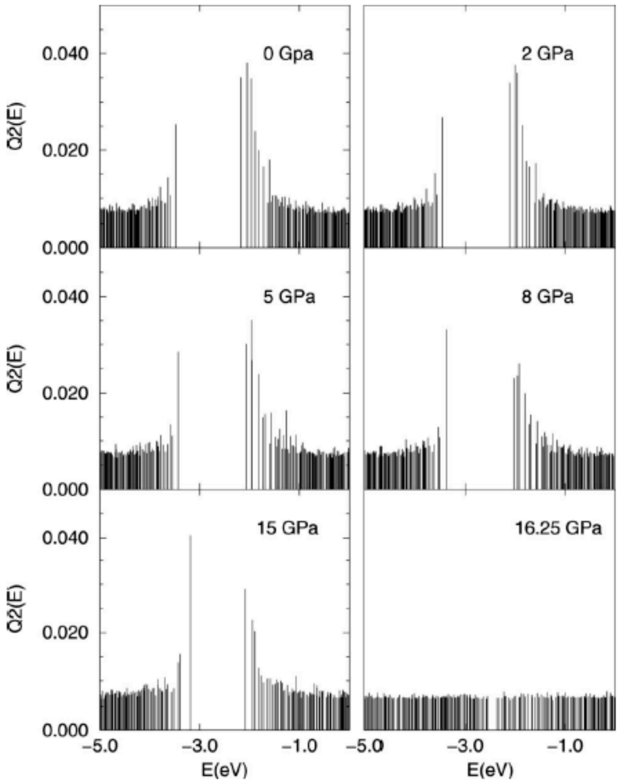


FIG. 6. Electronic eigenstates in the band gap region. The position of vertical bars represents the eigenvalues of the electronic eigenstates and height of the bars is the spatial localization $Q_2(E)$. The Fermi level lies in the middle of the band gap. Note the abrupt delocalization of tail states at 16.25 GPa.

Localization (Inverse Participation Ratio) and pressure. Note the abrupt delocalization of band tails at critical pressure and collapse of the gap

Binary glass - a different story

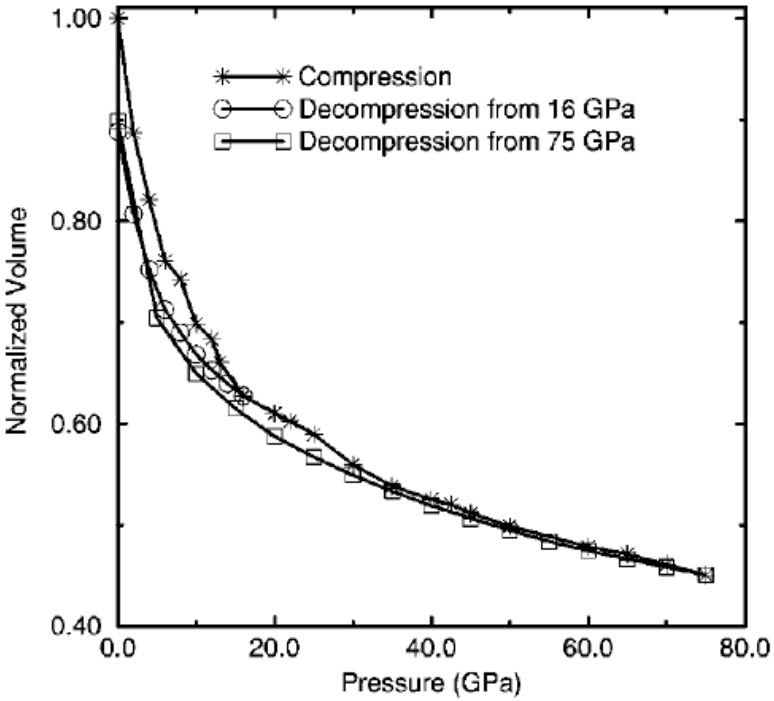


FIG. 1. The normalized volume of *a*-GeSe$_2$ changes smoothly with up to 12 GPa. After this pressure and several others, it shows slope changes. Upon a pressure release from 75 GPa, the path is reversed up to 30 GPa, and thereafter hysteresis is seen.

Glassy GeSe$_2$

Continuous transition!

Durandurdu, DD
PRB **65** 2002

Photo-response

- At every (MD) time step we have a lot of information: coordinates, energy eigenvalues, eigenfunctions, density matrix,…

We can simulate light-induced promotion (by changing electronic occupations) and monitor structural change from creating the pair.

Logic

Simulate an electron-hole pair (remove e^- from top of valence states n and add to bottom of conduction states n+1). For Hamiltonian H and electron states ψ

The net change in the interatomic ‘bandstructure’ force is:

$$\Delta F_\alpha = <\psi_{n+1}| -\partial H/\partial R_\alpha |\psi_{n+1}> - <\psi_n| -\partial H/\partial R_\alpha |\psi_n>$$

Force from occupying state n+1 (conduction tail)

Force from depleting state n (valence tail)

A 216-atom model of a-Se

Hybrid melt-quench with *a priori* information (chain topology)

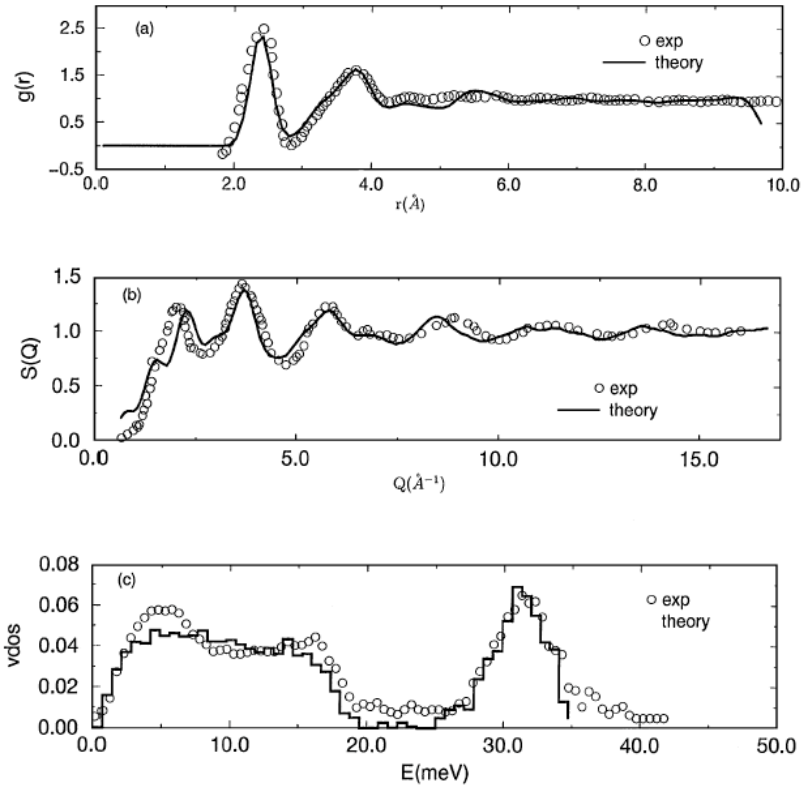


FIG. 1. Comparison between experiment and theory: (a) pair-correlation function $g(r)$; (b) static structure factor $S(Q)$; (c) vibrational density of states

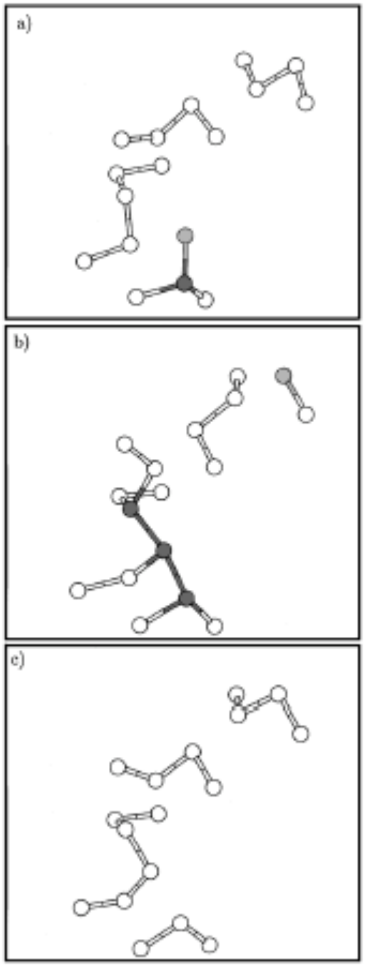
Example: Amorphous Se

- Starting structure (one IVAP). Only active atoms shown.

- Intermediate structure (in excited state)

- Final structure

Defect Free! “Photoanneal”



X. Zhang, DD PRL **83** 5042 (1999)

a-Se: photo-induced changes

Usually the network *improves* with occupation change (as here, IVAP disappears).

Why: Network “feels” changes near where the defects wavefunctions are localized (these are the states that suffer occupation change). Network is locally “annealed” .

Other words: *The electron-phonon coupling is large for localized states*.

Atta-Fynn, Biswas, DAD PRB **69** 545204 (2004)

Where to learn more

- R. M. Martin, *Electronic Structure, Basic Theory and Practical Methods*, Cambridge, 2004.
- Associated website with a wealth of links to most active research groups, software and pedagogic tools: *ElectronicStructure.org*
- Detailed treatment of many aspects of DFT: Parr and Yang, *Density Functional theory of Atoms and Molecules* Oxford, 1989.
- Molecular Dynamics: Allen and Tildesley, *Computer Simulation of Liquids*, Oxford 1989.