First-year physics seminars for faculty overviews of research, fall 2017 (aimed at first-year graduate students and advanced undergraduates, open to all) Wednesdays 9:30-10:20 in COB1 322 (Willow Room)

Aug 30: David Strubbe. "Finding order in disorder: theoretical studies of amorphous materials and excited-state forces for photovoltaics"
Sept 6: Venkattraman Ayyaswamy. "The exciting future of microplasmas: Role of computations"
Sept 13: Ajay Gopinathan
Sept 20: Dustin Kleckner
Sept 27: Bin Liu
Sep 29 colloquium is Roland Winston.
Oct 4: Jay Sharping
Oct 11: Chih-Chun Chien
Oct 18: Linda Hirst
Oct 20 colloquium is Jing Xu.
Oct 25:
Nov 1: Sayantani Ghosh
Nov 8: Lin Tian
Nov 15: Michael Scheibner
Nov 22 is a non-instructional day.
Nov 29: Kevin Mitchell
Dec 6:
Finding order in disorder: theoretical studies of amorphous materials and excited-state forces for photovoltaics

David A. Strubbe

Physics, University of California, Merced
My research

1. Amorphous materials

2. Excited-state dynamics

3. Methods and code development
What is it like to do computational condensed-matter theory?

Developing calculation approaches  
Implementation in computer code  
Running codes  
Analyzing results  
Comparing to experimental data  
Making simple models

What do you need to know?  
- Condensed matter physics  
- Quantum mechanics  
- Sometimes electrodynamics and statistical mechanics  
- Numerical methods, e.g. linear algebra and differential equations  
- Programming
Current students

Enrique Guerrero – amorphous silicon. Structure generation, interfaces, defects, voids

Kuntal Talit – hybrid perovskites. Electronic structure, vibrations, optical spectrum.

(CH$_3$NH$_3$)PbI$_3$
Collaborators

Amorphous silicon:
Gergely Zimányi, UC Davis (theory)
Frances Hellman, UC Berkeley (experiment)

Hybrid perovskites:
Sayantani Ghosh, physics (experiment)
Boaz Ilan, applied mathematics (theory)
Vincent Tung, materials science and engineering (experiment)

Methods and codes:
Steven Louie, UC Berkeley (theory)
Angel Rubio, Max Planck Institute for Structural Dynamics (theory)
Computation

Laptop, 8 cores

MERCED cluster, SE2 basement, ~2000 cores

Edison (100k) and Cori (600k) supercomputers, National Energy Research Supercomputing Center, Lawrence Berkeley National Laboratory, Berkeley, CA
Versatility of theory

• Scanning tunneling microscopy simulation
• Light-driven change of molecular structure
• Non-linear optics (second-harmonic generation) in liquids
• Conductivity of single-molecule devices
• Thermoelectricity in single-molecule devices
• Excitons in organic semiconductors
• Thermoelectricity in nanoporous silicon
• Raman spectroscopy and strain in amorphous silicon
• Photovoltaic effects in patterned functionalized graphene
• Solar energy storage by change in molecular structure
• Thermodynamic limits on solar energy capture and storage
Condensed-matter physics

Solid-state physics

- Liquids (e.g., superfluid helium)
- Hard condensed matter

- Soft condensed matter

- Atomistic
  - Quantum mechanics
  - First principles (ab initio)

- Continuum
  - Classical force fields
  - Semi-empirical, models, tight-binding
Basic theoretical technique: density-functional theory (DFT)

Quantum mechanics for electrons ("electronic structure"): time-independent Schrödinger equation

$$H \Psi = E \Psi \quad \Psi (r_1, r_2, \ldots)$$

Many-electron Hamiltonian:

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + V_{\text{ion}} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

One-electron Kohn-Sham Hamiltonian:

$$H_{\text{KS}} = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}} + \frac{1}{2} \int \frac{e^2 n}{|r - r'|}$$

$$\Psi (r_1, r_2, \ldots) = |\psi_1 (r_1) \psi_2$$

Reducing to effective one-electron problem
Time-dependent density-functional theory (TDDFT)

Time-dependent Schrödinger equation

\[ H \Psi = E \Psi \]

\[ H \Psi = -i\hbar \frac{d\Psi}{dt} \]

Start at non-equilibrium condition, propagate in time
Or, solve for excited states by response to oscillating electric field
Good for optical properties of molecules (including non-linear)

Density-functional perturbation theory

Response to perturbation (e.g. moving atoms).

\[ \frac{\partial}{\partial \lambda} |\psi_i\rangle = \sum_{i \neq j} |\psi_j\rangle \frac{\langle \psi_j | \frac{\partial H}{\partial \lambda} | \psi_i \rangle}{\epsilon_i - \epsilon_j} \]

S. Baroni, et al., Rev. Mod. Phys. 73, 515 (2001)
D. A. Strubbe et al., in Fundamentals of TDDFT (Springer, 2012)
**GW approximation/Bethe-Salpeter approach**

Start with DFT, treat exchange and correlation as a perturbation

GW self-energy: single-electron energy levels from Green’s function, screened Coulomb interaction (band structure, ionization potential, electron affinity)

\[ \Sigma = iGW \quad H^{\text{QP}} = H^{\text{DFT}} - V_{xc} + \Sigma \]

Bethe-Salpeter equation: electron-hole interaction (optical spectrum, excitons)

More computationally expensive than TDDFT but more generally applicable (solids)

\[ |A\rangle = \sum_{cv} a_{cv} |cv\rangle \quad H^{(2)} |A\rangle = \omega |A\rangle \]

Electronic structure methods

- **Density-functional theory (DFT)**
  - Cheap, good for structural properties, ground state

- **Time-dependent density-functional theory (TDDFT)**
  - Mid-price. Good for optical properties in molecules, not so good for solids

- **GW / Bethe-Salpeter Equation (BSE)**
  - Expensive, quasiparticle band structure, optical excitations. Generally accurate for all systems.

- **Quantum Monte Carlo (QMC)**
  - Extremely expensive, but accurate and general, for ground and excited states
Amorphous materials

- **Crystalline**: short- and long-range order (periodic)
- **Amorphous**: only short-range order

No single structure: continuum of variation

Non-equilibrium growth, sensitive dependence on conditions

Inhomogeneity, voids, coordination defects

Theory and experimental challenges: extended but non-periodic, long length scales

R. A. Street, *Hydrogenated Amorphous Silicon* (1991)
Amorphous Si

Photovoltaics, transistors, MEMS, batteries. Hydrogenated to passivate dangling bonds (a-Si:H)

Long-studied model amorphous system (other amorphous semiconductors and insulators)

Raman spectroscopy is key characterization tool: crystallization, order, temperature, interfaces, strain, ...
Theory helps in interpretation.

20% efficient dopant-free asymmetric heterojunction (DASH) cell
J. Bullock et al., Nature Energy 1, 15031 (2016)
Stress: properties and characterization

Stress from deposition, processing, nanostructuring

Affects properties, e.g. electron mobilities in a-Si:H

H. Gleskova et al., Appl. Phys. Lett. 79, 3347 (2001)

Raman microscopy characterization: stress alters vibrational frequencies (e.g. c-Si optical phonon)


Inconclusive theory and experiment for a-Si
Raman spectroscopy

Light creates (or destroys) vibrations through excited states

Raman tensor from polarizability derivative with respect to atomic positions

\[ R_i = \frac{\partial \alpha}{\partial r_i} \]
Amorphous structure generation

Not a single structure – big structures, statistical sampling and averaging required
“WWW method” : classical Monte Carlo method


Add H\textsubscript{2} to initial lattice to produce a-Si:H with \sim 10\% H

D. A. Strubbe, L. K. Wagner, E. J. Johlin, and J. C. Grossman, CHASSM code
(Computational Hydrogenated Amorphous Semiconductor Structure Maker)
Raman spectrum: theory vs. experiment

- 4-point bending rods
- c-Si wafer

Shifts with applied strain

TO

0.5% uniaxial strain

0.3% uniaxial stress

exp't neutral

exp't compressive

c-Si

theory compressive

theory neutral

theory tensile

Raman shift (cm\(^{-1}\))

Raman intensity (arb. units)

tensile

compressive

Comparing strain coefficients

Strain in exp’t inferred from c-Si shift

\[ \Delta \omega^c = \left( -330 \pm 70 \text{ cm}^{-1} \right) \epsilon_{xx} \]

Theory: \( s = -460 \pm 10 \text{ cm}^{-1} \)
Experiment: \( s = -500 \pm 100 \text{ cm}^{-1} \)


Conclusions (I)

First *ab initio* calculation of Raman spectrum of a-Si:H, in agreement with experiment

Methods work well for this property

Strain calibration for micro-Raman strain mapping, confirmed by agreement of new theory/exp’t

Pentacene: an organic semiconductor

Applications: thin-film transistors, photovoltaics, and optoelectronics.

Model organic crystal semiconductor

Self-trapped exciton forms

Important for excitonic transport, perhaps singlet fission: $S \rightarrow T + T$
(get two electrons for one photon)

Stokes shift = 0.19 eV

Optical absorption spectrum of pentacene

Lowest singlet exciton 1.7 eV

Long-ranged charge transfer to neighboring molecules. Need GW/BSE to describe correctly.

Self-trapped excitons

$\alpha$-quartz ($\text{SiO}_2$)

Stokes shift = 6 eV

Si-O bond breaks (red = Si, blue = O)

Finite differences would require $3N$ calculations. Total scaling $O(N^6)$!

Excited-state forces in Bethe-Salpeter equation

\[ E_1 = E_0 + \omega \]

derivatives with respect to atomic displacements

\[ F = -\partial E_1 = -\partial E_0 - \partial \omega \]

DFT ground-state forces

\[ |A\rangle = \sum_{cv} a_{cv} |cv\rangle \]

\[ |A\rangle = \text{excited state} \]
\[ \nu = \text{valence, occupied, hole} \]
\[ c = \text{conduction, unoccupied, electron} \]

\[ H^{(2)} |A\rangle = \omega |A\rangle \]
Excited-state forces in BSE: new approach

Previous approach (schematically):

\[ \partial \omega = \sum_{cvc'v'} a_{cv}^* \langle cv | \partial \left[ \sum_{c''v''} |c''v''\rangle \langle c''v'' | H^{(2)} \sum_{c'''v'''} |c'''v'''''\rangle \langle c'''v''''' | \right] |c'v'\rangle a_{c'v'}^* \]


Derivatives from density-functional perturbation theory (as for a-Si:H phonons) with some approximations for computational feasibility

New approach (Hellman-Feynman Theorem):

\[ \partial \omega = \sum_{cvc'v'} a_{cv}^* \langle cv | \partial H^{(2)} |c'v'\rangle a_{c'v'}^* \]


No need for extra summations on unoccupied states
Improved accuracy, efficiency, scaling

Also: more accurate and consistent approximation of GW derivatives
Forces on pentacene singlet exciton

~0.1 eV/Å

Similar distortion needed for singlet fission in pair calculations

P. M. Zimmermann et al., J. Am. Chem. Soc. 133, 19944 (2011)
Conclusions (II)

Reformulation of excited-state forces from the Bethe-Salpeter equation for improved efficiency and convergence. Only mean-field derivatives required.

Access to self-trapped excitons, Stokes shifts, etc. Implemented in freely available BerkeleyGW code.

Distortion from singlet exciton of pentacene crystal: molecular rotation.

Photovoltaics

Best Research-Cell Efficiencies

Multijunction Cells (2-terminal, monolithic)
- LM = lattice matched
- IM = metamorphic
- IN = inverted, metamorphic
  - Three-junction (concentrator)
  - Three-junction (non-concentrator)
  - Two-junction (concentrator)
  - Two-junction (non-concentrator)
  - Four-junction or more (concentrator)
  - Four-junction or more (non-concentrator)

Single-Junction GaAs
- Single crystal
- Concentrator
- Thin-film crystal

Crystalline Si Cells
- Single crystal (concentrator)
- Single crystal (non-concentrator)
- Multicrystalline
- Silicon heterostructures (HIT)
- Thin-film crystal

Thin-Film Technologies
- CZTSSe (concentrator)
- CIS
- CdTe
- Amorphous Si:H (stabilized)

Emerging PV
- Dye-sensitized cells
- Perovskite cells (not stabilized)
- Organic cells (various types)
- Organic tandem cells
- Inorganic cells (CZTSe)
- Quantum dot cells (various types)

Efficiency (%)

- a-Si/c-Si tandem HIT 28%
- Perovskites (not stabilized) 22%
- a-Si:H (stabilized) 14%
- Organic cells (various types) 11.5%

https://www.nrel.gov/pv/assets/images/efficiency-chart.png
Light-induced degradation of hybrid perovskites

What kind of defect states are being created?
How can we design a more stable material or device?

Wanyi Nie et al., Nat. Commun. 7, 11574 (2016)