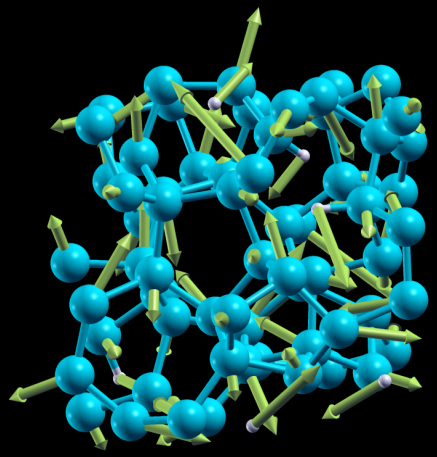
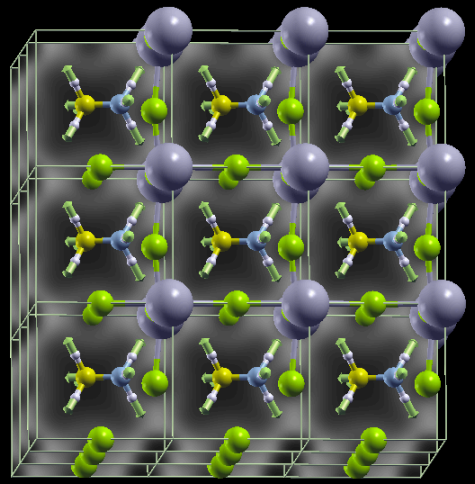
First-year physics seminars for faculty overviews of research, fall 2017
(aimed at first-year graduate students and advanced undergraduates, open to all)
Wednesdays 9:30-10:20 in COB1 322 (Willow Room)

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
Sept 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



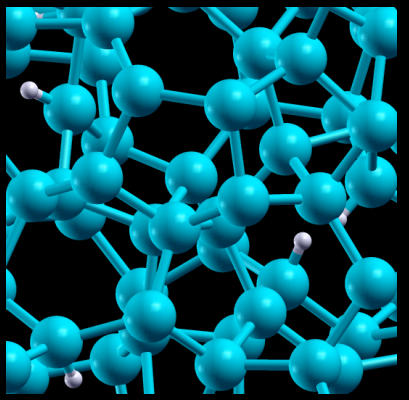


UC MERCED
UNIVERSITY OF CALIFORNIA

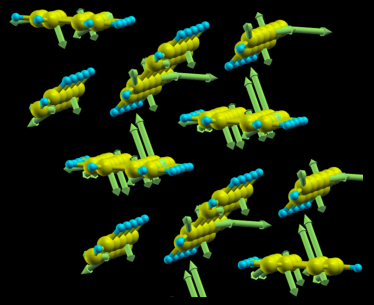
First-Year Student Seminar, UC Merced Physics
30 August 2017

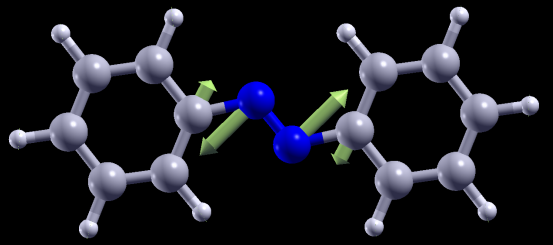
My research

1. Amorphous materials

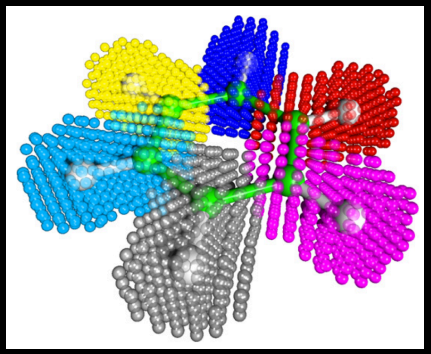


2. Excited-state dynamics





3. Methods and code development



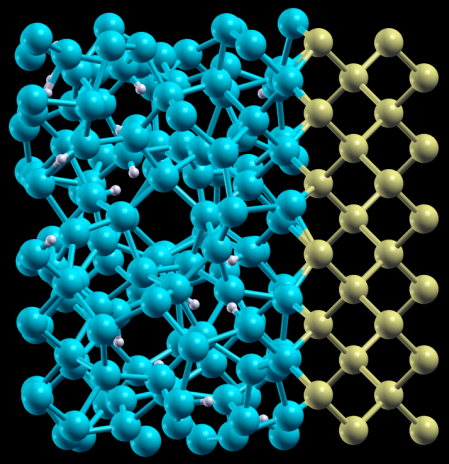
What is it like to do computational condensed-matter theory?

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

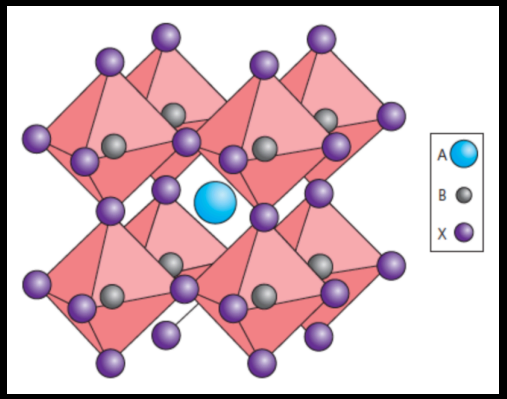
What do you need to know?
- Condensed matter physics
- Quantum mechanics
- Sometimes electrodynamics and statistical mechanics
- Numerical methods, e.g. linear algebra and differential equations
- Programming

Current students

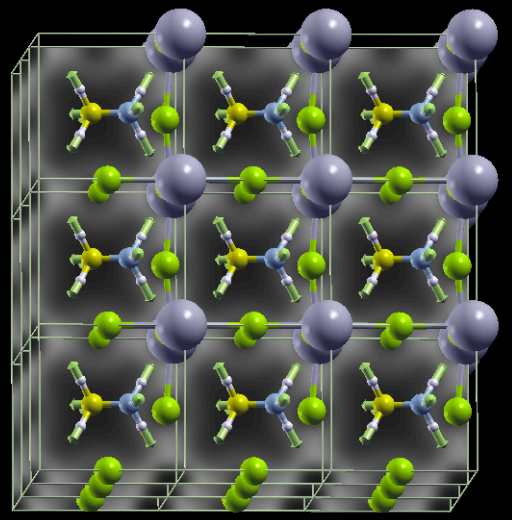
Enrique Guerrero – amorphous silicon. Structure generation, interfaces, defects, voids



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



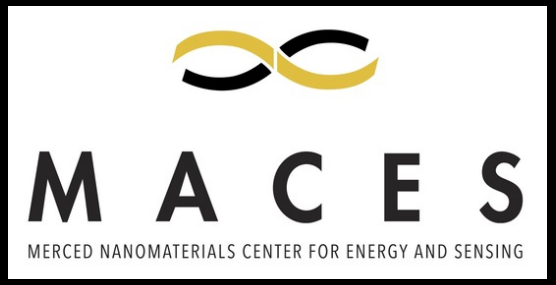
$(CH_3NH_3)PbI_3$

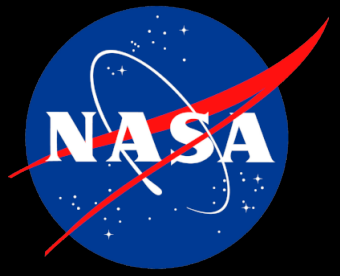


Collaborators

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)

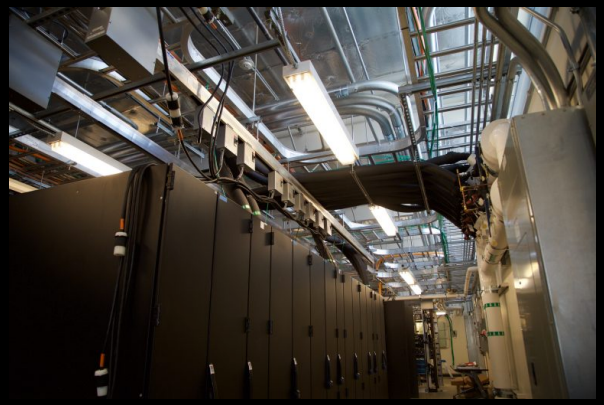


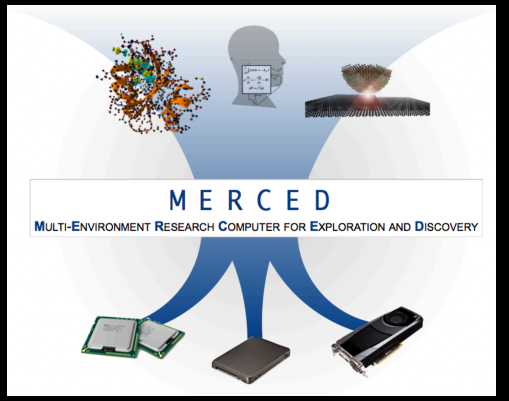


Methods and codes:
Steven Louie, UC Berkeley (theory)
Angel Rubio, Max Planck Institute for Structural Dynamics (theory)

Computation

Laptop, 8 cores





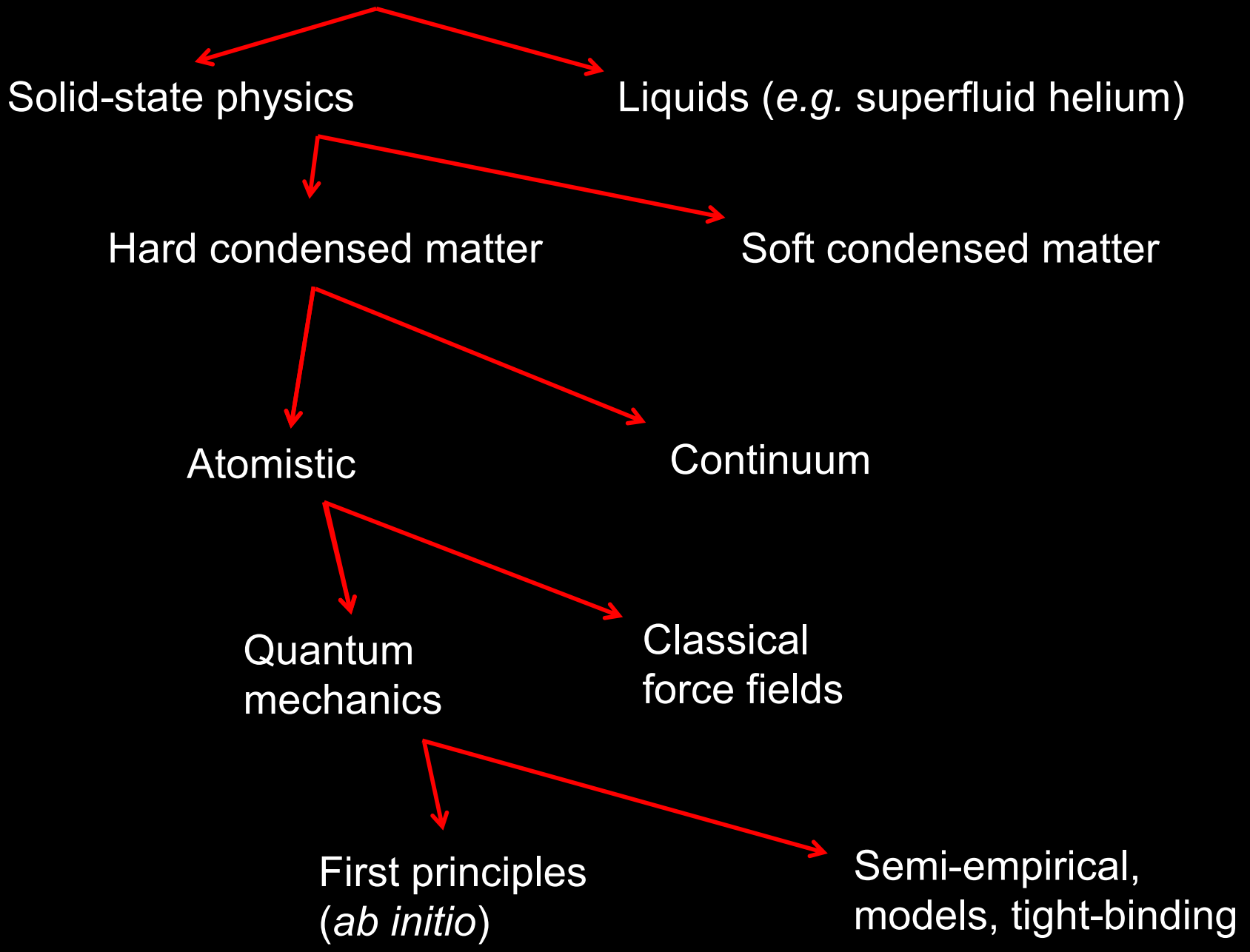
MERCED cluster, SE2 basement, ~2000 cores

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



Basic theoretical technique: density-functional theory (DFT)

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

$$H\Psi = E\Psi \qquad \Psi\left(r_1, r_2, \ldots\right)$$

$$O\left(e^N\right)$$

Many-electron Hamiltonian:

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

One-electron Kohn-Sham Hamiltonian:

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

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

Reducing to effective one-electron problem

Time-dependent density-functional theory (TDDFT)

Time-dependent Schrödinger equation

$$H\Psi = E\Psi \longrightarrow H\Psi = -i\hbar\frac{d\Psi}{dt}$$

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).

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

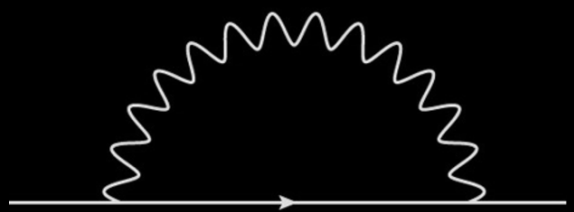
S. Baroni, *et al.*, *Rev. Mod. Phys.* **73**, 515 (2001)
D. A. Strubbe *et al.*, in *Fundamentals of TDDFT* (Springer, 2012)

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)

$$\Sigma = iGW \qquad H^{\mathrm{QP}} = H^{\mathrm{DFT}} - V_{\mathrm{xc}} + \Sigma$$

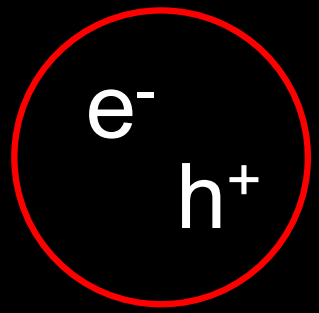


$$\epsilon^{-1}\left(r, r', \omega\right) \frac{1}{|r - r'|}$$

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

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

$$|A\rangle = \sum_{cv} a_{cv} |cv\rangle \qquad H^{(2)} |A\rangle = \omega |A\rangle$$



Mark S. Hybertsen and Steven G. Louie, *Phys. Rev. B* **34**, 5390 (1986)
Michael Rohlfing and Steven G. Louie, *Phys. Rev. B* **62**, 4927 (2000)

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)

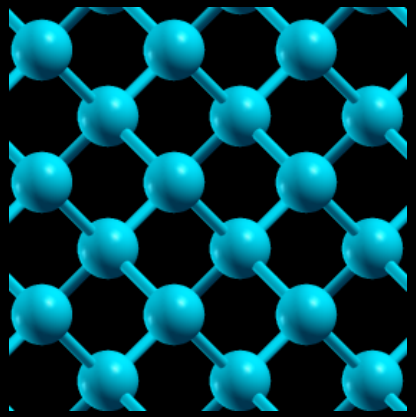
Expensive, quasiparticle band structure, optical excitations. Generally accurate for all systems.

Quantum Monte Carlo (QMC)

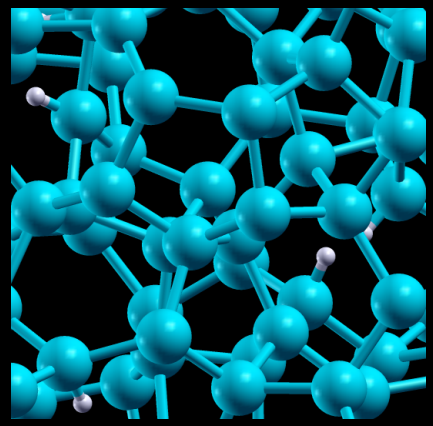
Extremely expensive, but accurate and general, for ground and excited states

Amorphous materials

crystalline:
short- and long-range order (periodic)



amorphous:
only short-range order

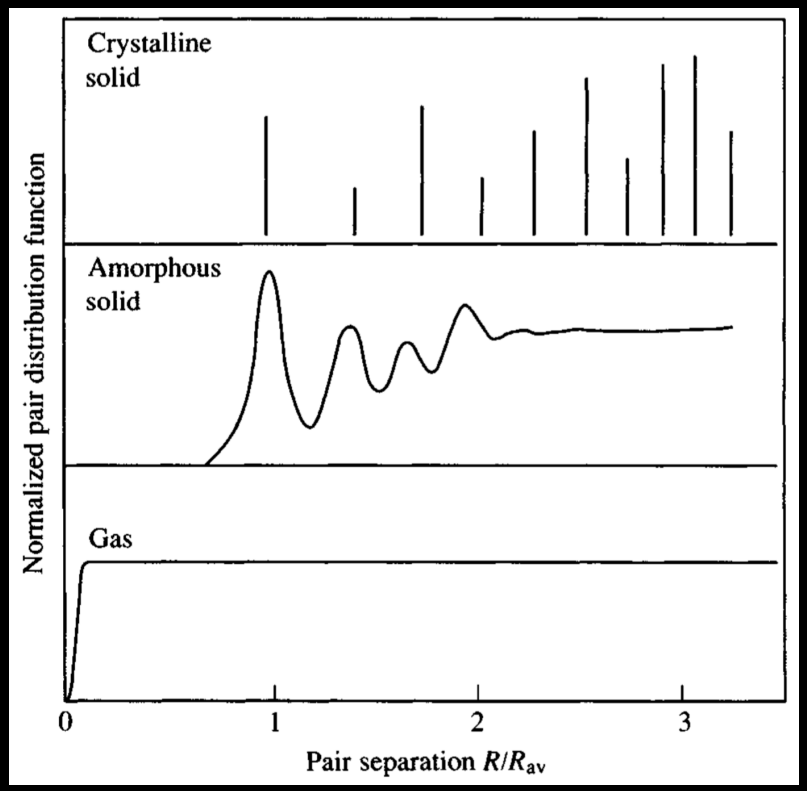


No single structure: continuum of variation

Non-equilibrium growth, sensitive dependence on conditions

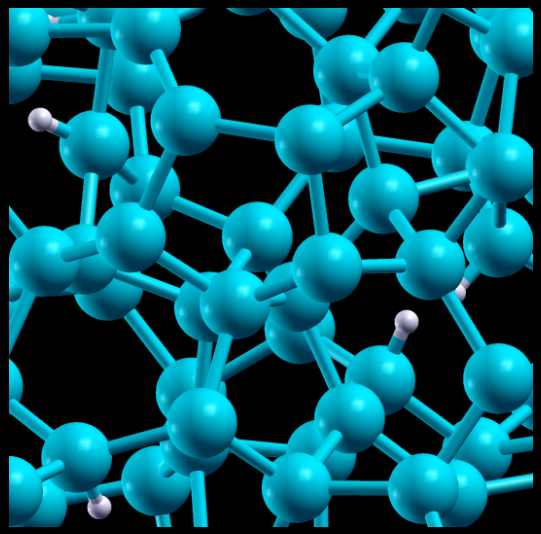
inhomogeneity, voids, coordination defects

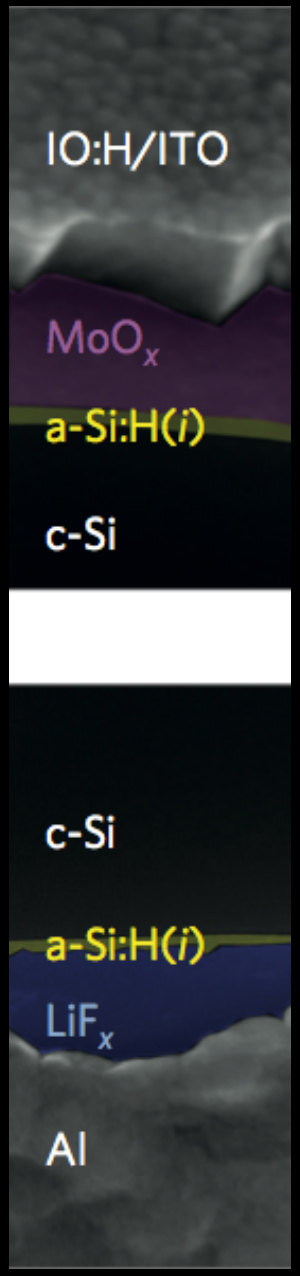
Theory and experimental challenges:
extended but non-periodic, long length scales



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.

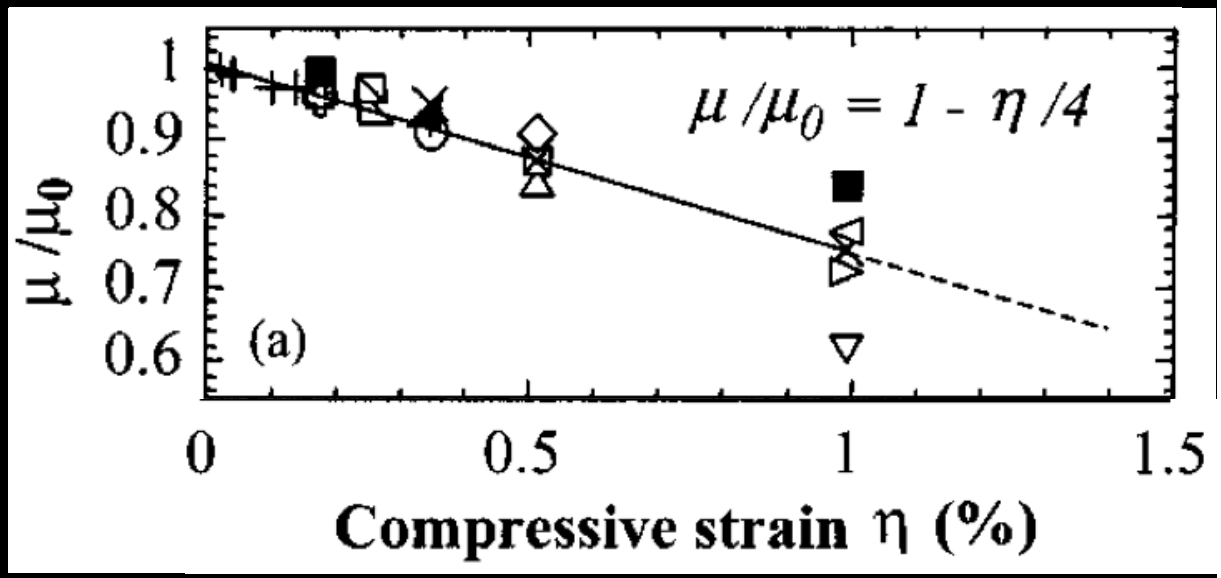
20% efficient dopant-free asymmetric heterojunction (DASH) cell
J. Bullock *et al., Nature Energy* **1**, 15031 (2016)

Stress: properties and characterization

Stress from deposition, processing, nanostructuring

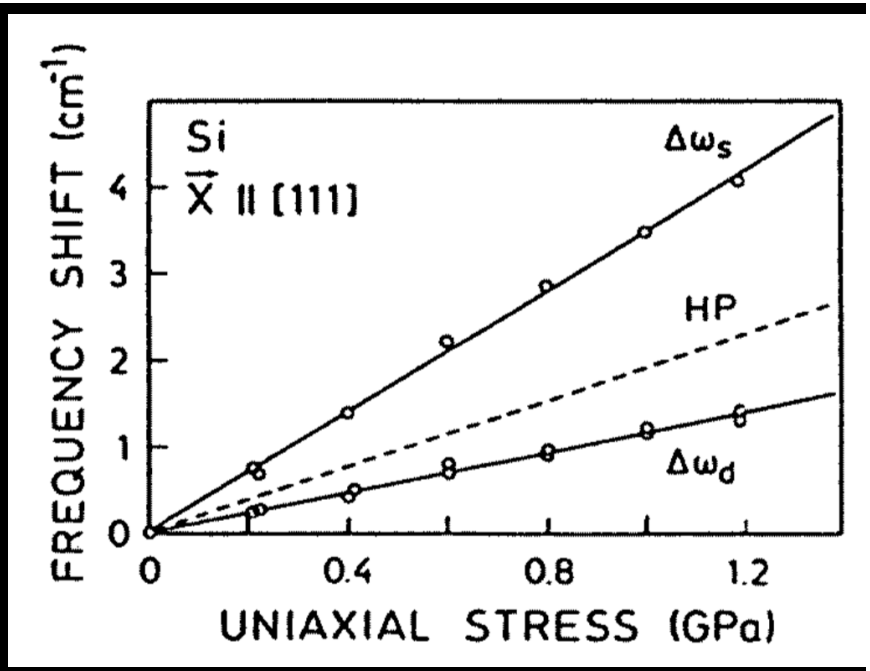
Affects properties, *e.g.* electron mobilities in a-Si:H

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



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

I. de Wolf, *Semicond. Sci. Technol.* **11**, 139 (1996)
E. Anastassakis *et al.*, *Solid State Commun.* **8**, 133 (1970)



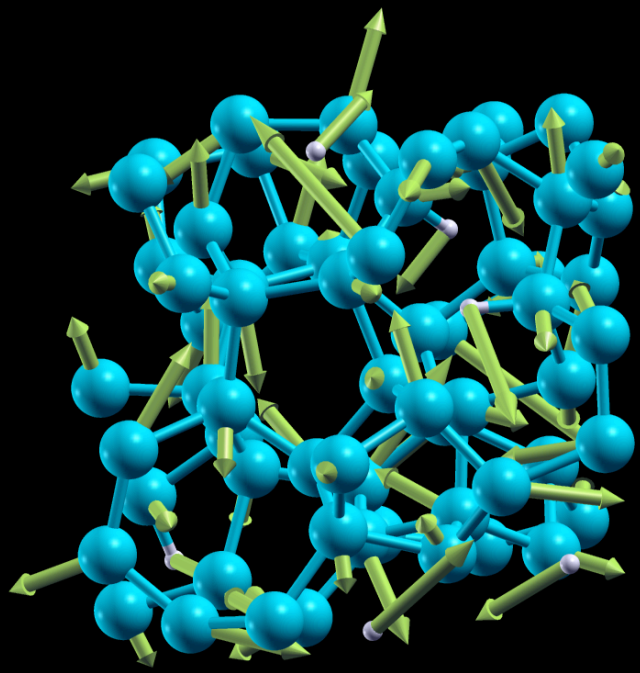
Inconclusive theory and experiment for a-Si

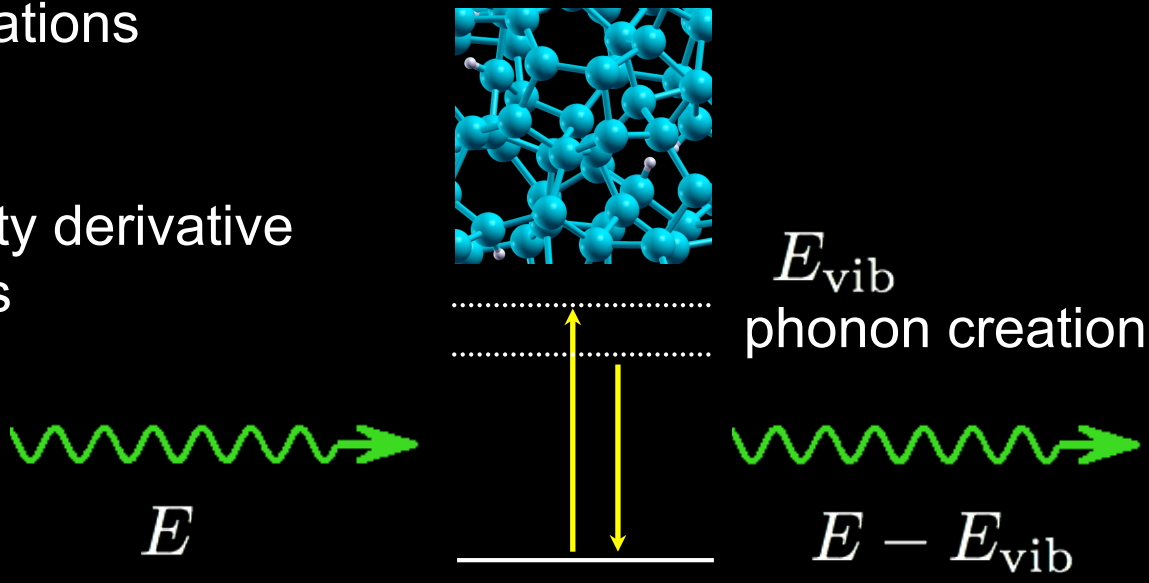
Raman spectroscopy

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

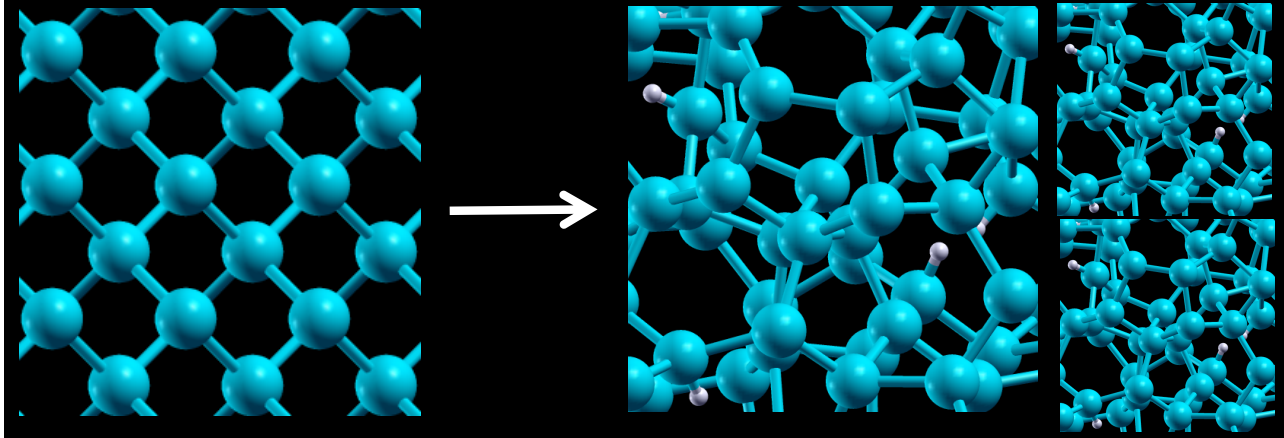
"WWW method" : classical Monte Carlo method

F. Wooten, K. Winer, and D. Weaire, *Phys. Rev. Lett.* **54**, 1392 (1985)

Add H_2 to initial lattice to produce a-Si:H with ~10% H

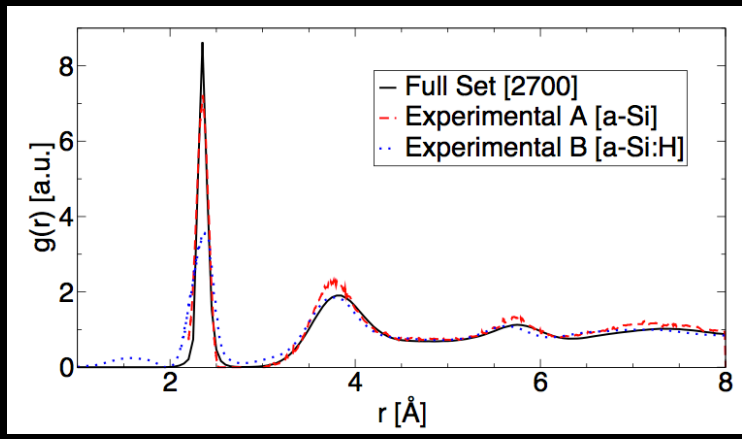
E. J. Johlin, L. K. Wagner, and J. C. Grossman, *Phys. Rev. Lett.* **110**, 146805 (2013)

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

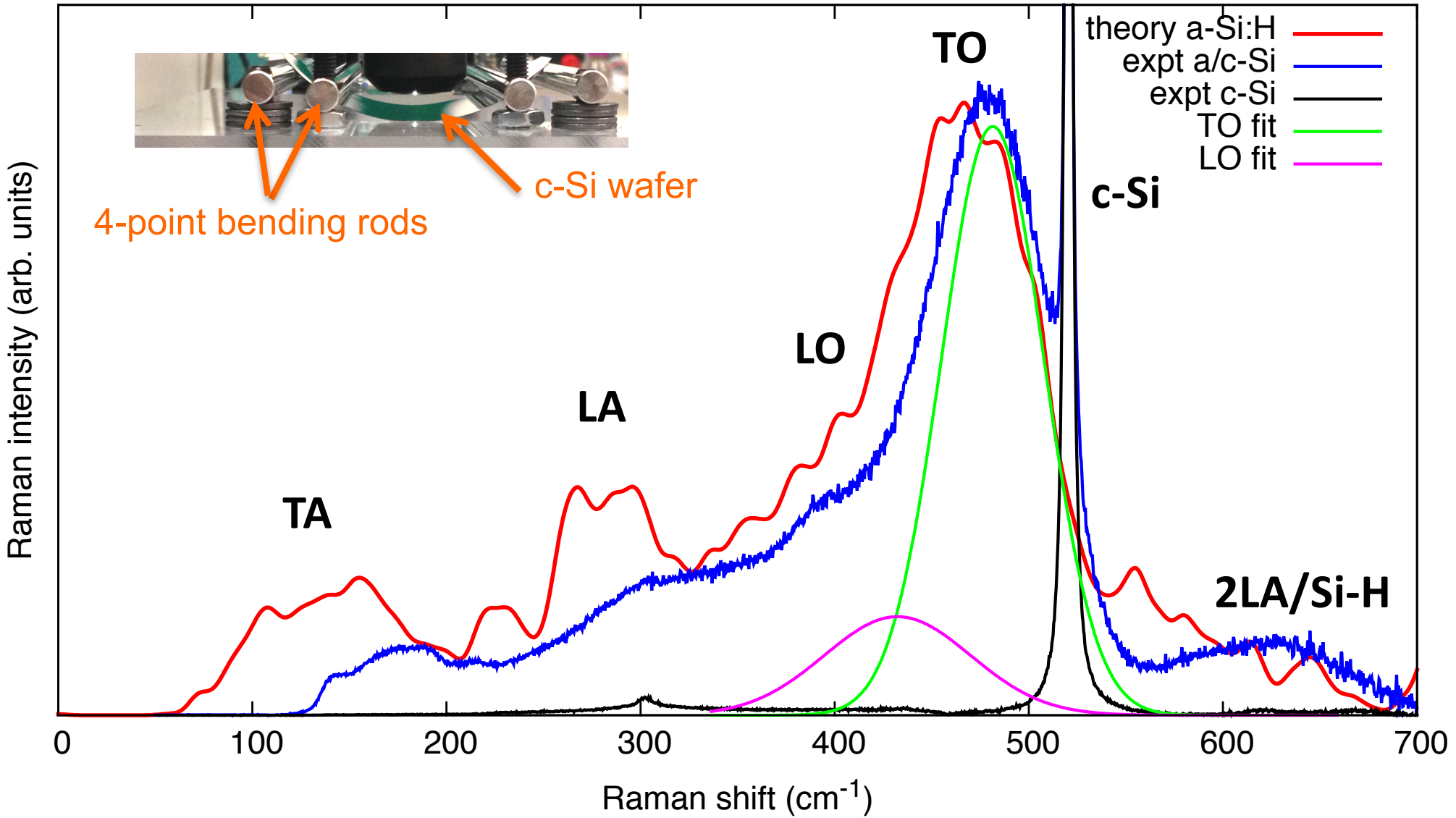


c-Si

34 structures of $Si_{64}H_6$

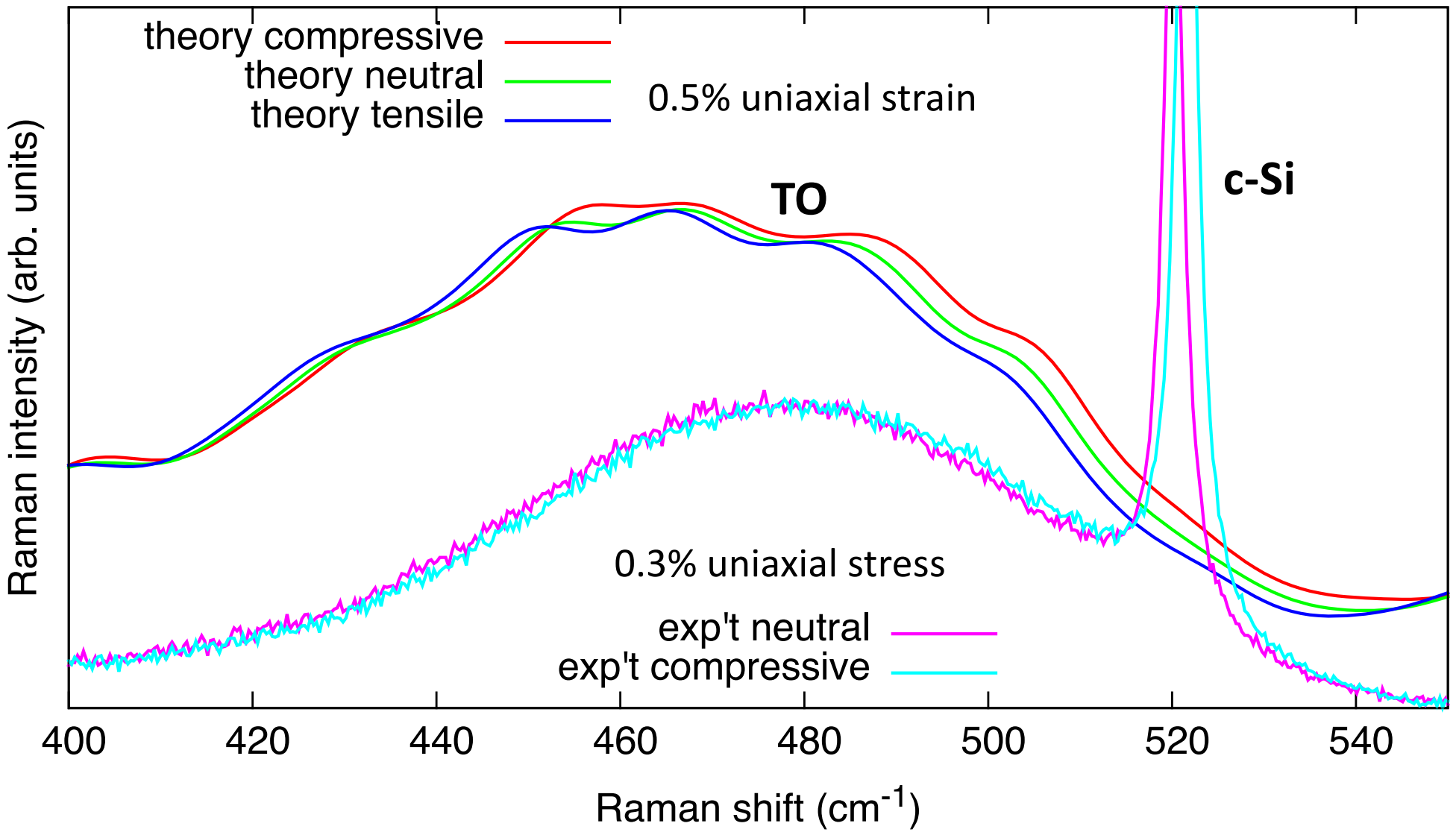


Raman spectrum: theory *vs*. experiment



D. A. Strubbe, E. C. Johlin, *et al.*, *Phys. Rev. B* **92**, 241202(R) (2015)

Shifts with applied strain



tensile ⟵ ⟶ compressive

D. A. Strubbe, E. C. Johlin, *et al.*, *Phys. Rev. B* **92**, 241202(R) (2015)

Comparing strain coefficients

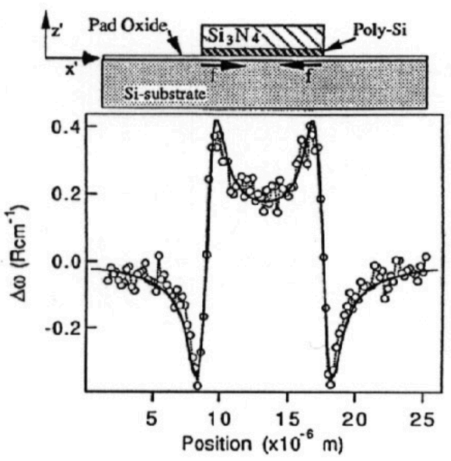
Strain in exp't inferred from c-Si shift

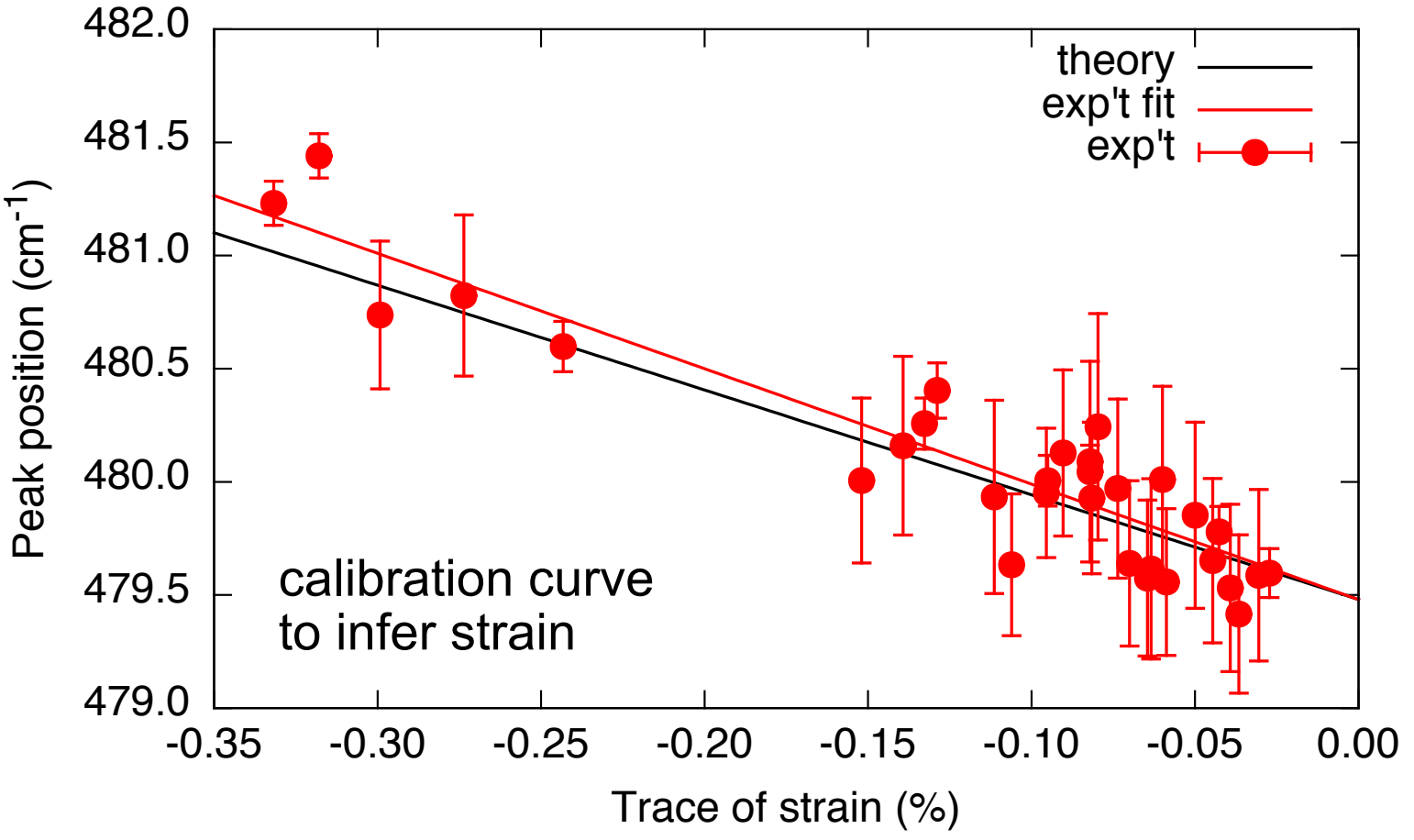
$$\Delta\omega^c = \left(-330 \pm 70\ \mathrm{cm}^{-1}\right)\epsilon_{xx}$$

E. Anastassakis *et al.*, *Solid State Commun.* **8**, 133-138 (1970)

Theory: s = -460 ± 10 cm^{-1}

Experiment: s = -500 ± 100 cm^{-1}

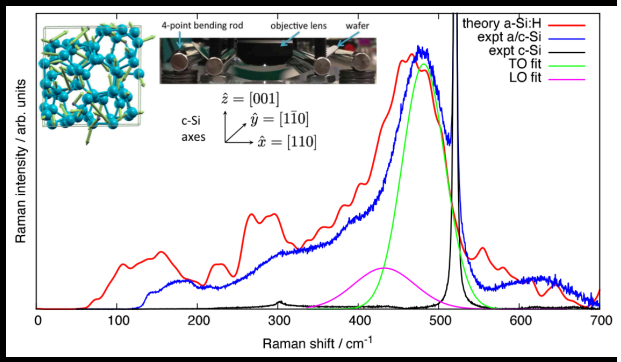




D. A. Strubbe, E. C. Johlin, *et al.*, *Phys. Rev. B* **92**, 241202(R) (2015)

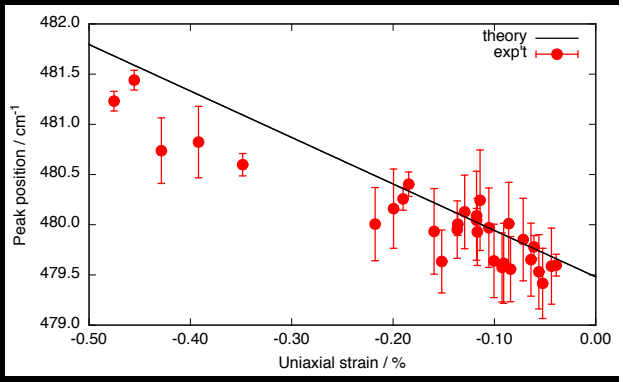
Conclusions (I)

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



D. A. Strubbe, E. C. Johlin, T. K. Kirkpatrick, T. Buonassisi, and J. C. Grossman, *Phys. Rev. B* **92**, 241202(R) (2015)

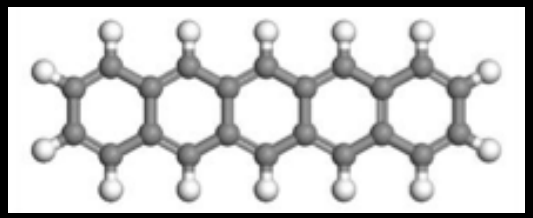
Pentacene: an organic semiconductor

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

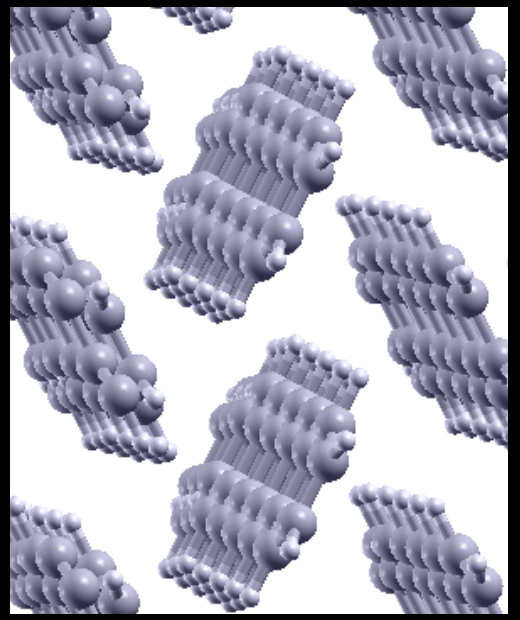
Model organic crystal semiconductor

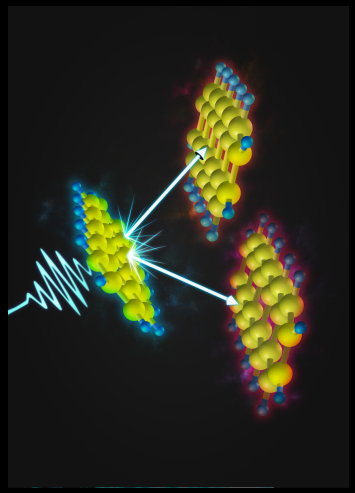
Self-trapped exciton forms

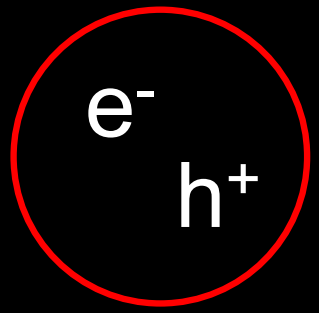
Important for excitonic transport, perhaps singlet fission: S → T + T (get two electrons for one photon)

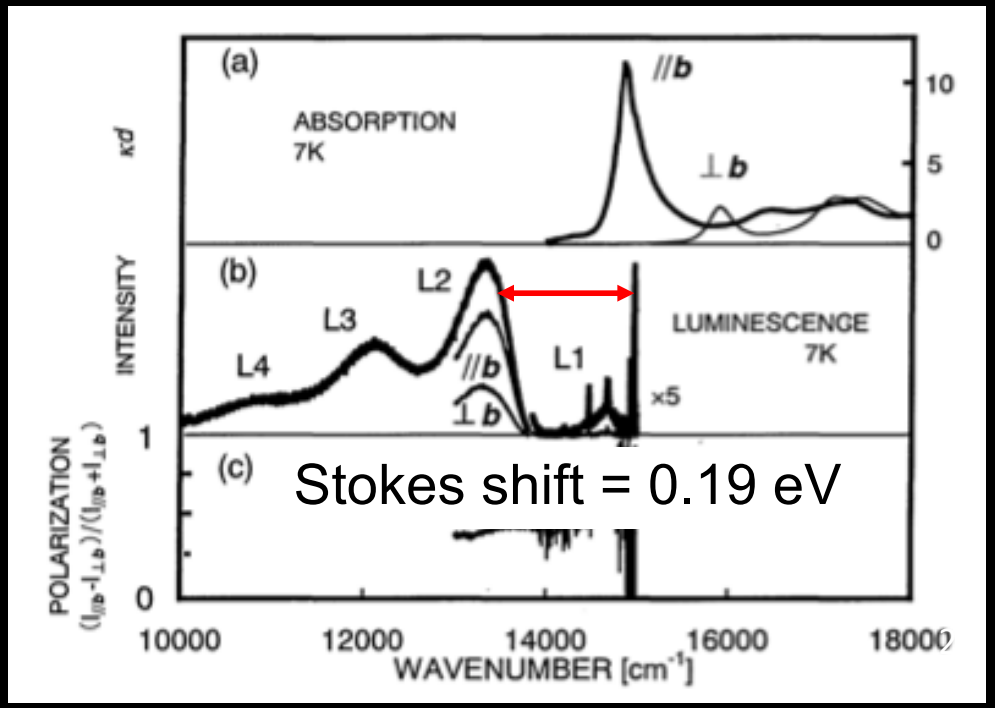


2 molecules,
72 atoms / cell



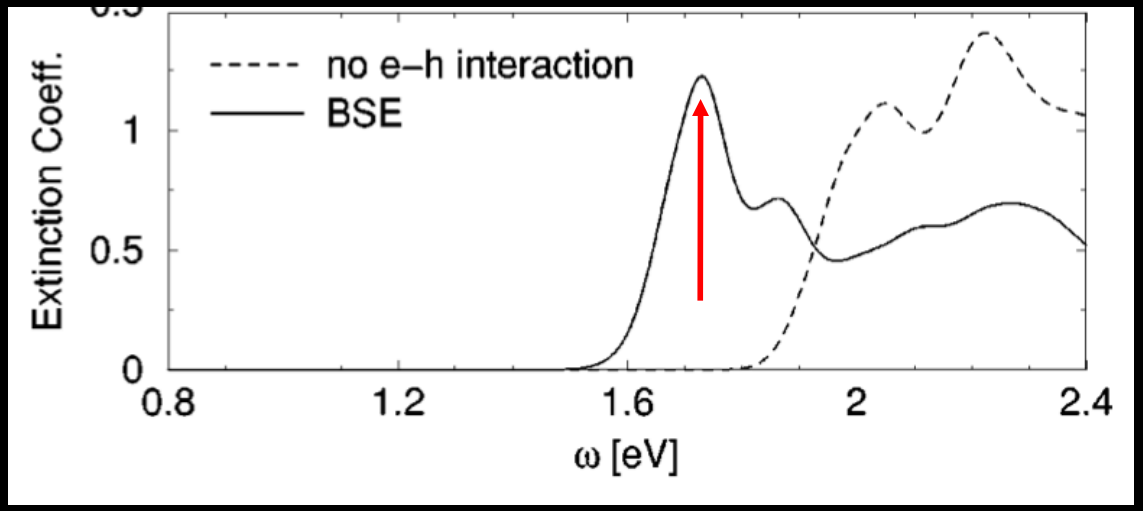


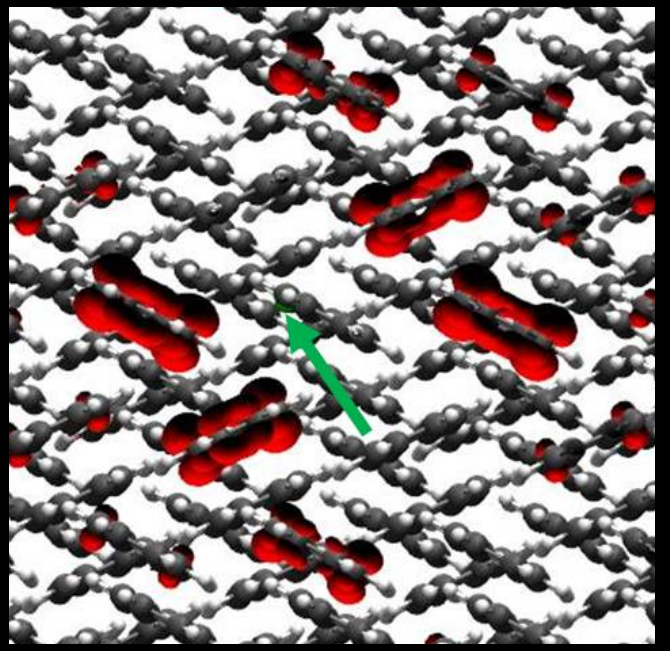




T. Aoki-Matsumoto *et al.*, *Int. J. Mod. Phys. B* **15**, 3753 (2001)

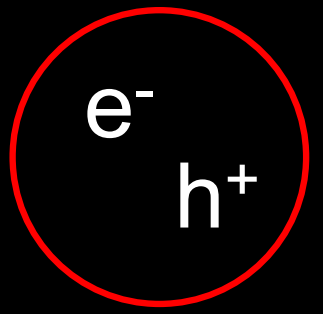
Optical absorption spectrum of pentacene





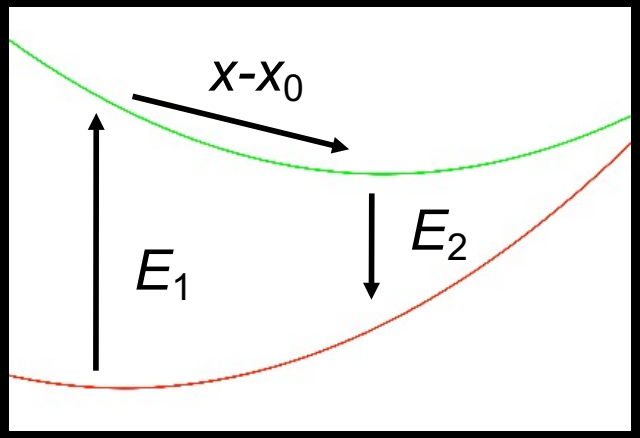
Lowest singlet exciton 1.7 eV

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



ML Tiago, JE Northrup, and SG Louie, *Phys. Rev. B* **67**, 115212 (2003)
S Sharifzadeh, A Biller, L Kronik, and JB Neaton, *Phys. Rev. B* **85**, 125307 (2012)

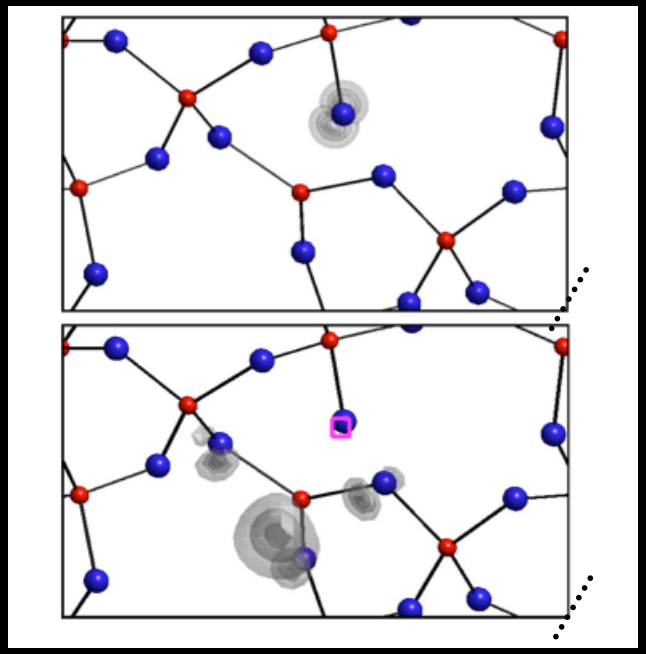
Self-trapped excitons



Stokes shift = E_1 - E_2

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

α-quartz (SiO_2)



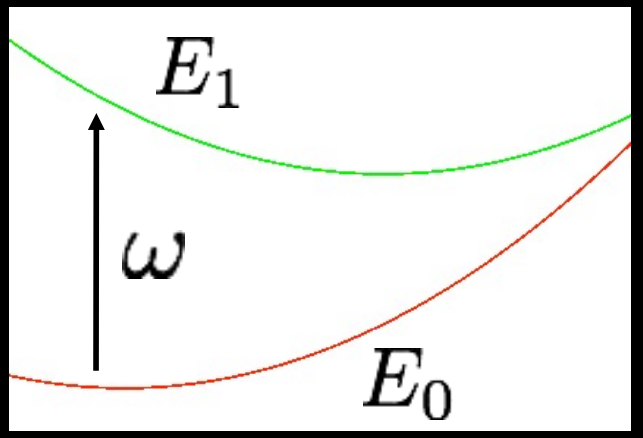
Si-O bond breaks
(red = Si, blue = O)

Stokes shift = 6 eV

Sohrab Ismail-Beigi and Steven G. Louie, *Phys. Rev. Lett.* **95**, 156401 (2005)

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

$$|A\rangle = \sum_{cv} a_{cv} |cv\rangle$$

$|A\rangle$ = excited state

v = valence, occupied, hole

c = conduction, unoccupied, electron

$$H^{(2)} |A\rangle = \omega |A\rangle$$

Excited-state forces in BSE: new approach

Previous approach (schematically):

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

Sohrab Ismail-Beigi and Steven G. Louie, *Phys. Rev. Lett.* **90**, 076401 (2003)

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

New approach (Hellman-Feynman Theorem):

$$\partial\omega = \sum_{cvc'v'} a^*_{cv} \langle cv| \partial H^{(2)} |c'v'\rangle a^*_{c'v'}$$

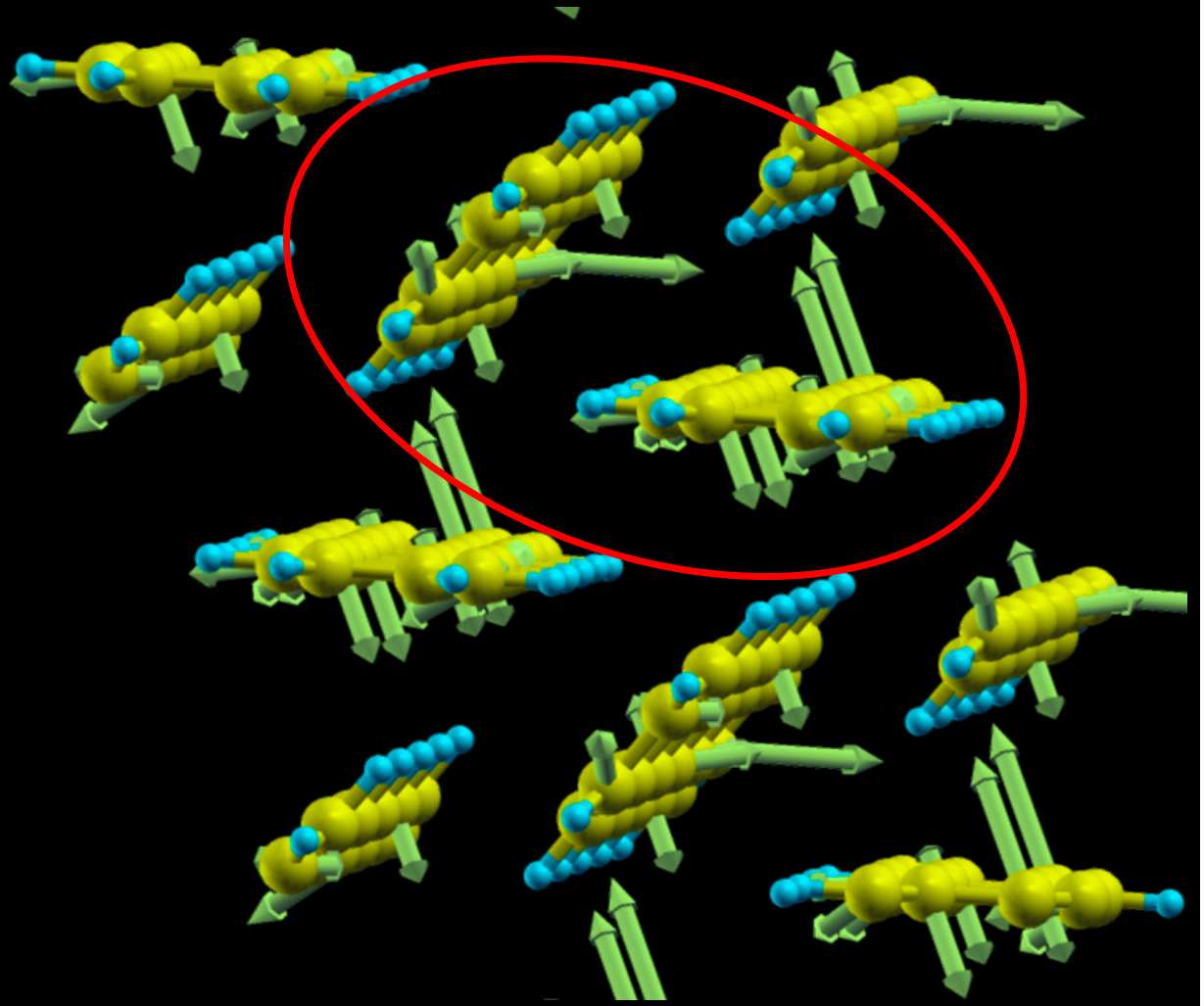
David A. Strubbe, Ph.D. thesis, University of California, Berkeley (2012)

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

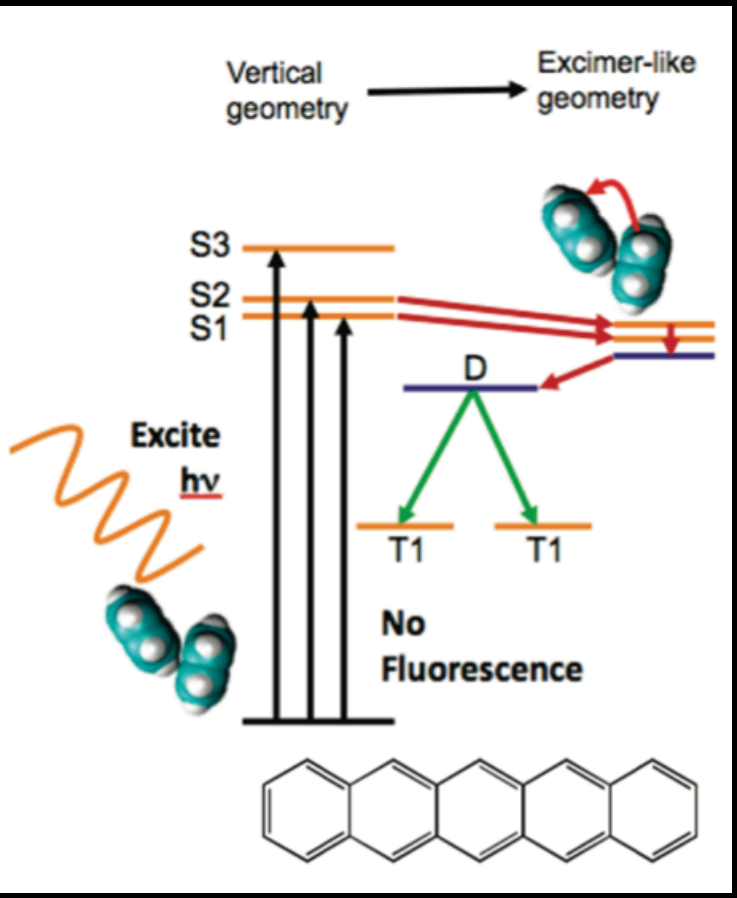
Also: more accurate and consistent approximation of *GW* derivatives

Forces on pentacene singlet exciton

~0.1 eV/Å



Similar distortion needed for singlet fission in pair calculations



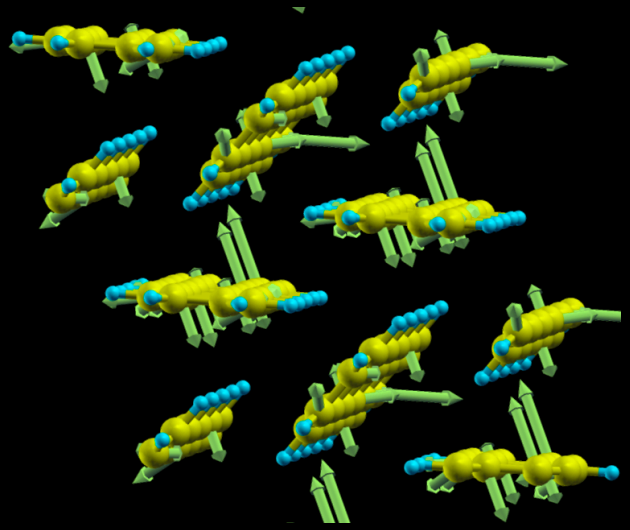
P. M. Zimmermann *et al., J. Am. Chem. Soc.* **133**, 19944 (2011)

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.

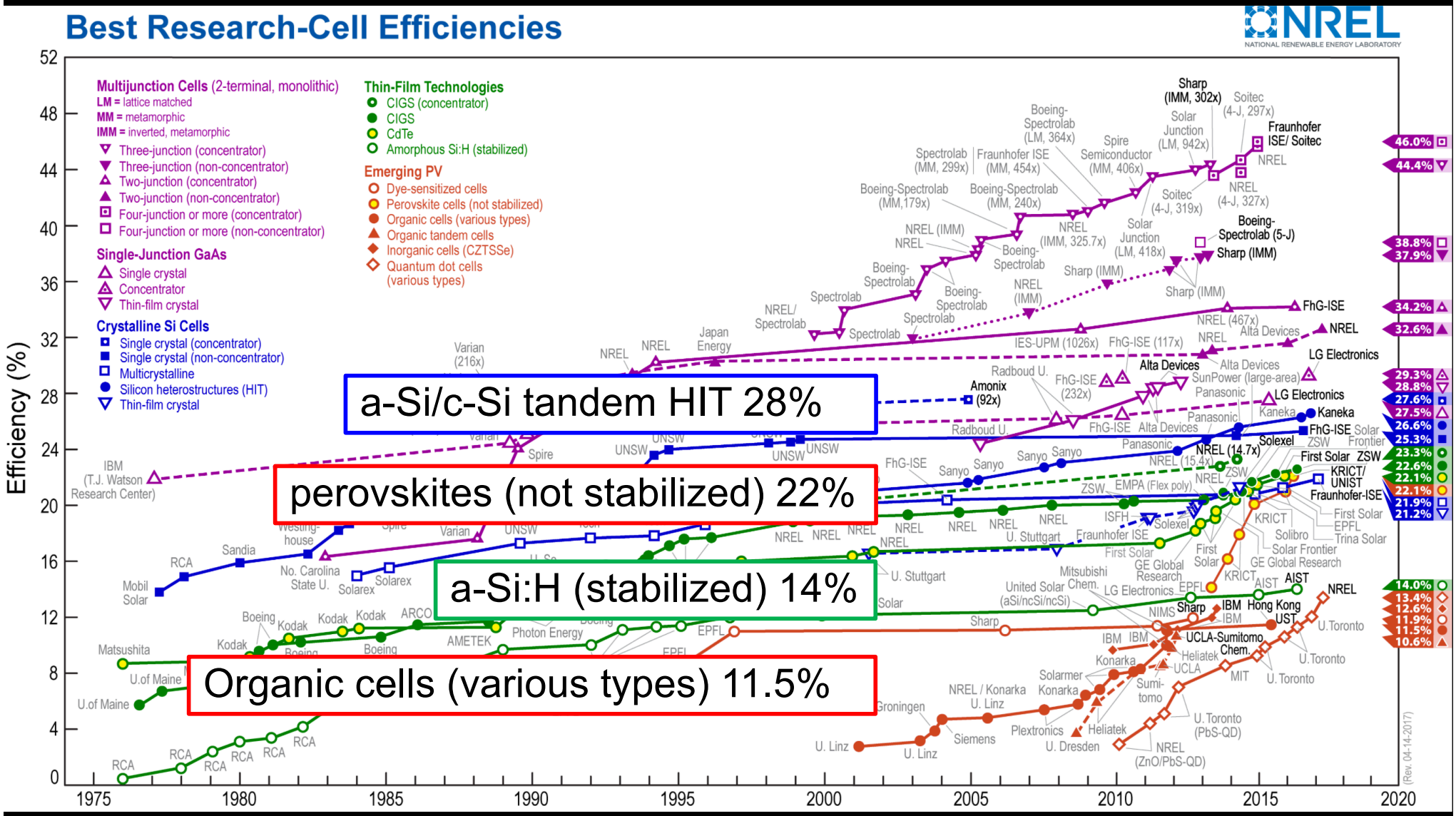
Distortion from singlet exciton of pentacene crystal: molecular rotation.



BerkeleyGW

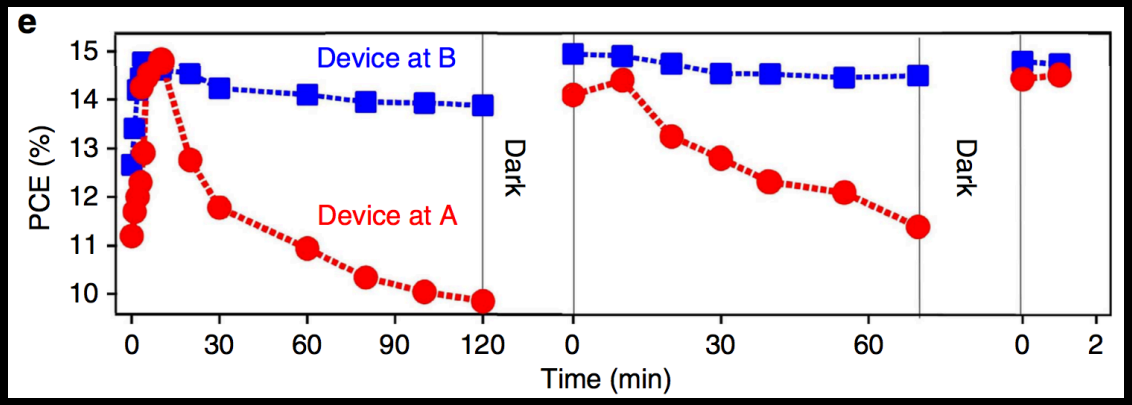
J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, *Comput. Phys. Comm.* **183**, 1269 (2012); www.berkeleygw.org

Photovoltaics

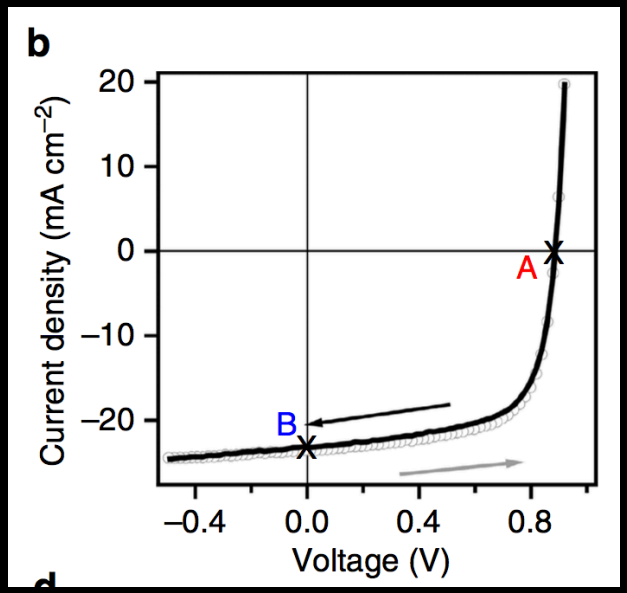


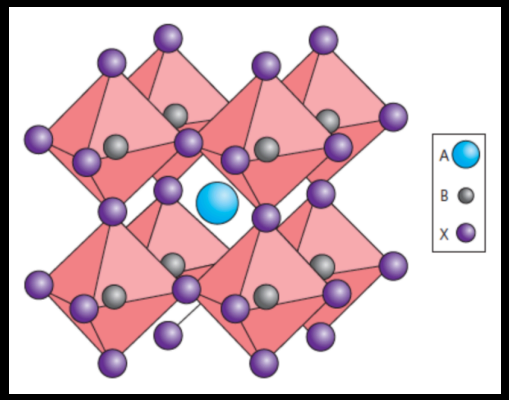
https://www.nrel.gov/pv/assets/images/efficiency-chart.png

Light-induced degradation of hybrid perovskites

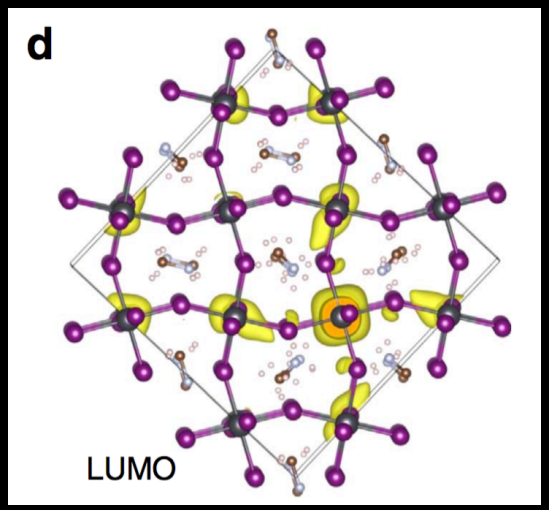


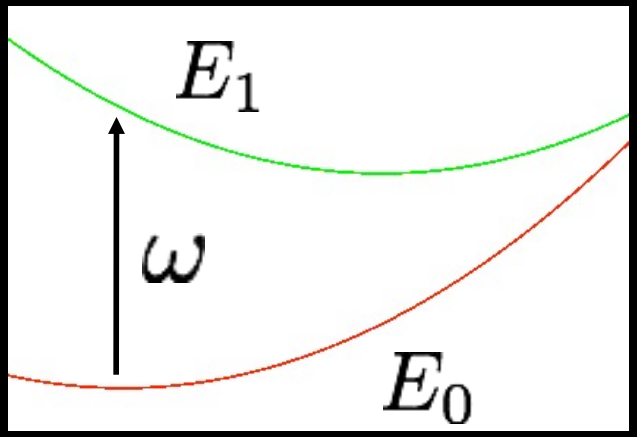
Wanyi Nie *et al.*, *Nat. Commun.* 7, 11574 (2016)





$(CH_3NH_3)PbI_3$





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