Understand, predict and design nanostructured materials: insight from quantum simulations

Giulia Galli
University of California, Davis
Outline

• Challenges and opportunities in theoretical and computational materials science

• Predictive computations of multiple properties with controllable accuracy

• Materials for energy
  • Optical and thermoelectric properties of nanostructured materials

• Outlook
Exciting opportunities in materials science

• Development of advanced materials is a key element for creating new technologies for, e.g. efficient and sustainable energy supplies

• Advanced materials are complex!
  — Pressing call for theory and computation in “realistic environments”
  — Need for reliable, microscopic descriptions of matter

Investigate materials from their basic constituents: electrons and nuclei

\[ H\psi = E\psi \]
Predictive modeling of multiple properties with controllable accuracy

- Accuracy of approximate \textit{ab-initio} methods
- Efficiency of \textit{ab-initio} methods ("the length scale problem")

- \textit{Ab-initio} electronic structure methods combined with sampling techniques
- Multiple, coupled probes for multiple properties
- Understanding, predictions, design and experimental validation

- Efficiency of sampling techniques to describe dynamics and rare events ("the time scale problem")

- Coupling of techniques, coarse graining, message passing ...
Predictive modeling of multiple properties

Classical Molecular Dynamics (MD):

Ground State properties: Structural, electronic, some thermodynamic and dynamical properties

Ab-initio Molecular Dynamics (MD):

Accuracy

Ground State properties: Structural, electronic, some thermodynamic and dynamical properties

Time scales

Quantum Monte Carlo:
Optical Gaps and Total Energies

Excited State properties

Many Body Perturbation Theory:
Spectra, Correlation energies

Effective Hamiltonians for Monte Carlo simulations:
Defects in solids and entropy

Thermodynamic properties

Accelerated MD:
Nucleation processes

Rare events and transport properties

Boltzmann equation:
Heat transport

T.Li, D.Donadio, L.Ghiringhelli, G.G Nat.Mat. 2009 and JCP 2009
D.Donadio and G.G., PRL 2007, PRL 2009, NL 2010

Predictive modeling of multiple properties

Ab-initio Molecular Dynamics (MD):

Ground State properties: Structural, electronic, some thermodynamic and dynamical properties

Efficiency

Where do we stand? ~ 700 e⁻/~ 100 ps; 5000 e⁻/ ~ps
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Search for materials for photovoltaic applications: Opto-electronic properties of Silicon

**Light emission from nanoparticles (NP)**
- Where does it come from?
- Interplay between quantum confinement and defects?
- Differences between colloidal and matrix-precipitated NPs?

**Light absorption in dots and rods**
- Can we optimize absorption in functionalized Si-rods so as to use them as efficient photocathodes for solar cells?

**Multi-exciton generations**
- Origin and dependence on preparation conditions and structure of particles?


Optical properties of Si nanocrystals beyond size `reduction` (or quantum confinement)

- **H-terminated Si dots (~ 2nm):** ‘step’-like reconstruction unique to highly curved surfaces, responsible for optical gap and excitonic lifetime reduction
- **Presence of oxygen or nitrogen** greatly affects optical gap below 2 nm (gap reduction), as well as Stoke shifts

![Optical Absorption Gap vs. Q-Dot Diameter](chart)

- **For amorphous dots,** presence of oxygen may lead to gap increase
- **Chemical reactivity** at the surface may be greatly increased by photo-excitation

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Key influence of surface structure and passivation on opto-electronic properties

Key role of first principles approach in elucidating interplay between structure and `function`

High energy excitations of Si nanoparticles (NP)

Time-dependent density functional (TDDFT) calculations of excitation spectra:

• Surface reconstruction may change excitation spectra both at low and high energies above the gap

• Absorption may be enhanced non-linearly by the presence of alkyl groups, and by the interaction between NPs.

• Insight into interpretation of experiments on Multi-Electron-Generation in colloidal NPs.


Time dependent Kohn-Sham equations

\[ i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t) = \left[ -\frac{1}{2} \nabla^2 + v_H(\mathbf{r}, t) + v_{xc}(\mathbf{r}, t) + v_{ext}(\mathbf{r}, t) \right] \phi_i(\mathbf{r}, t) \]
Optical properties of solids and nanostructures, including excitonic effects

- Full spectrum at a computational cost comparable to several Hartree-Fock ground state calculations
- Calculations of empty electronic states, full dielectric matrix, inverse of dielectric matrix (and basis set approximations) avoided
- Method suitable for large basis sets and large systems

Systems of size comparable to experiments, e.g. Si dots in the few nm range

Charge transfer excitations: e.g. in dipeptides

Si$_{35}$H$_{36}$

- Full BSE
- TDA BSE

\[ I(\omega) \]

\[ \omega \text{ [eV]} \]

Nanostructures in realistic environments

- Nanoparticles embedded in solid matrices
- Nanoparticles in solutions

Inorganic and inorganic/organic interfaces

- Si dot in SiNx
- Thiol protected Au$_{102}$
- CdSe in solution

CNT/AFM tip in solvent


Structural models for embedded Si nanoparticles

- We have used simulation techniques similar to those employed to study nucleation in supercooled l-Si (*), in order to precipitate Si nanoparticles in silicon nitride and oxide amorphous matrices
  — at present feasible only with semi-empirical potentials
- We have investigated interface structures and computed electronic properties using ab-initio techniques

Electronic identity of embedded nanoparticles is not well defined


Nanostructures in realistic environments:

- Nanoparticles **embedded in solid matrices**
- Nanoparticles in **solutions**
Microscopic properties of organic-inorganic interface investigated by first principle calculations

Full system calculation (Qbox\textsuperscript{[1]})

Complementary calculations (PWSCF\textsuperscript{[2]})

MBA, MT/Au(111)

Isolated Au\textsubscript{102} cluster

1596 atoms
6924 electrons

DFT/PBE,
Norm-conserving pseudopotentials
plane-wave basis, ecut=75 Ry


\textsuperscript{[1]} Qbox code: http://eslab.ucdavis.edu/software/qbox
\textsuperscript{[2]} PWSCF code: http://www.pwscf.org
Microscopic properties of organic-inorganic interface investigated by first principle calculations

Ability to simulate the exact system investigated experimentally

1596 atoms
6924 electrons

Semiconductor with a sizeable gap

Organics on metals are usually `difficult` cases for DFT/GGA

• Proper treatment of dispersion forces is often a key element in determining equilibrium geometries of Self Assembled Monolayers (SAMs):

  - Ongoing studies using EXX/RPA (*)

\[
E_c = \frac{1}{2\pi} \int_0^\infty du \sum_q \sum_i \{\log[\varepsilon_i(q,iu)] - \varepsilon_i(q,iu) + 1\}
\]

• Electronic level alignment at the interface is seldom correctly described by DFT with local or semi-local functionals

• For example, for PDI/Au(111), many body perturbation theory (GW) results provide a qualitatively different picture of electron transport than calculations at the semi-local DFT level (**)

\[
\varepsilon_{GW}^{Ad}(j) = \varepsilon_{DFT}^{Ad}(j) + \Delta\Sigma_{GW}^{SAM} + \int_{z>z_c} [V_{im}(z) - V_{xc,DFT}(z)] \rho_{DFT}^{SAM}(j)
\]


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Thermoelectric properties at the nanoscale

Can nanostructuring help to improve efficiency in harvesting thermal energy?

- **Power generation** (Seebeck effect): maintain $\Delta T$ and convert heat into current

- **Cooling** (Peltier effect): Supply electrical current and pump (transfer) heat


Thermoelectric properties at the nanoscale

Can nanostructuring help to improve figure of merit, ZT?

Electrical conductivity

Figure of merit

$$ZT = \frac{\sigma S^2}{\kappa_e + \kappa_l} T$$

Seebeck coefficient = \frac{\Delta V}{\Delta T}

Electronic thermal conductivity

Ionic thermal conductivity


Design materials with high figure of merit by using semiconductor nanostructures

Observed efficiency not well understood—different interpretations provided by different groups; some reproducibility issues
Design materials with high figure of merit by using semiconductor nanostructures

- $S \sigma$ and $k_e$ from *ab-initio* calculations within Density Functional Theory (DFT).

- $k_i$: How do we compute thermal conductivity?

Si Nanowires: T.Vo, A.Williamson, V.Lordi and G.G. Nanolett. 08; D.Donadio, G.G. PRL 09 and NL 2010


Carbon Nanotubes: D.Donadio and G.G. PRL 07
Several techniques are available to compute $\kappa$

- **Green-Kubo formulation and calculation of heat current from equilibrium** Molecular Dynamics (MD)
  \[
  \kappa = \frac{1}{VK_bT^2} \int_0^\infty \langle J(t)J(0) \rangle dt
  \]

- **Non-equilibrium MD to compute heat flux (or temperature gradient) from applied temperature gradient (or heat flux)**
  \[
  \kappa = -\frac{1}{2tL_xL_y} \sum_{\text{transfers}} \left( \frac{m}{2} (v_n^2 - v_c^2) \right)
  \]

- **Boltzmann Transport Equation (BTE) to compute deviation of phonon occupation distribution from equilibrium distribution**
  \[
  -v_{\mathbf{z},i} \cdot \nabla T \frac{\partial n_i}{\partial T} + \left( \frac{\partial n_i}{\partial t} \right)_{\text{collision}} = 0, \quad \left( \frac{\partial n_i}{\partial t} \right)_{\text{collision}} = \frac{n_{i,\text{eq}} - n_i}{\tau_{i,r}}
  \]

- **Green’s functions approach: Landauer-Buttiker transmission function formalism**
  \[
  \sigma = \int_0^\infty \frac{\hbar \omega}{2\pi T} \left( \frac{d f_{\text{BE}}(\omega)}{dT} \right) d\omega.
  \]

Comparison between different approaches yet unclear—none of these techniques can be easily applied to *ab-initio* Hamiltonians.
Shape and surface structure strongly affect values of thermal conductivity of Si NWs

Classical MD

\[ k = \frac{1}{V k_b T^2} \int_0^\infty \langle J(t) J(0) \rangle dt \]

- **Size reduction** may not substantially decrease thermal conductivity \((\kappa)\) below bulk values
- **Surface structure** plays a major role in heat transport at the nanoscale
- **Non propagating, diffusive modes** are major heat carriers in wires with disordered surfaces, with a small contribution of low frequency phonons to \(\kappa\) (analysis from BTE and Allen-Feldman theory)
- Combination of dimensionality reduction and presence of disorder leads to ‘peculiar’ \(\kappa(T)\) dependence in Core-Shell wires

D. Donadio and G. G. PRL 2009 and Nanolett. 2010
Figure of merit of 3nm Si nanowires

3 nm wires: high ZT (> 1) may be attained if ionic thermal conductivity can be lowered by about 2 orders of magnitude wrt Si bulk.

\[ ZT = \frac{\sigma S^2}{\kappa_e + \kappa_l} T \]

3 nm; assume \( \kappa_l \sim 2 \text{ W/mK} \)

Strong dependence on surface structure and growth direction.

Important differences between n- and p-doping.

Recent experimental results (*) indicate such a lowering of \( \kappa_l \) may be possible.


T. Vo A. Williamson, V. Lordi and G.G., Nanolett. 08
Unusually low thermal conductivity reported for $\text{WS}_2$ thin films

Problem: layered chalcogenides are difficult to dope, hence electronic conductivity is very low.

Is there a way to “force” doping at the nanoscale?

C. Chiritescu et al., Science 2007
MoS$_2$ nanowires may be doped with Mo and made conductive

Tianshu Li and G.G. JPC-C (2007)
A.Splendiani, T.Li, G.G. and F. Wang, NL (submitted)
Work in progress

• Dielectric properties of thin films

• Methane dissociation and formation of hydrocarbons

• Materials for the environment
  - Water and aqueous solutions

Si₃N₄
Exciting opportunities in theoretical and computational materials science

• Development of **advanced materials** is a **key** element for creating new technologies for, e.g. **efficient and sustainable energy supplies**
• It is an exciting time to make a difference!

-Agreement with experiment is never a sufficient condition to judge simulation results; in certain instances it may be misleading

-Distinction between theory and numerical techniques is essential and increasingly overlooked
Davide Donadio (UCD), Yuping He (UCD), Ivana Savic (UCD)

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Tianshu Li, Yan Li, Deyu Lu, Dario Rocca, H-V Nguyen, Leonardo Spanu (UCD)

Adam Gali (U.Budapest, Hungary), Gergely Zimanyi (UCD)

G.Cicero (Turin, Italy)

Manu Sharma (UCD)

E.Schwegler (LLNL)

Francois Gygi (UCD)

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