Predicting complex materials properties: first principles calculations

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ANL, QMC Training Program, July 17th, 2014
Fundamental science and materials design

Photovoltaics

Solar to fuel

Thermoelectrics

Carbon cycle

Clean Water

CCI Powering the planet: http://www.ccisolar.caltech.edu/

Deep Carbon Observatory: http://deepcarbon.net/

http://ime.uchicago.edu/features/the_global_challenge_access_to_clean_fresh_water/
Complex semiconductors and insulators for energy conversion processes

- Can nanostructuring semiconductors help to beat the Shockley-Queisser limit in solar energy conversion?

- How do we engineer optimal transport channels for electrons and holes in a photoexcited material?

- How do we engineer optical gaps & band edges in phoelectrodes for water oxidation?

- Are charge and phonon transport in nanostructured thermoelectrics fundamentally different than at the macroscopic scale?
Complex semiconductors for energy conversion processes

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Excited states and transport properties

• Theoretical and computational strategies

• Short stories on solar energy conversion
  — Embedded nanoparticles
  — Si-based clathrates & perovskites
  — Photo-electrodes for water catalysis
Theoretical and computational strategy

Ab-initio MD and electronic structure calculations (GGA, VdW and hybrid DFT)
Structural models, trends in electronic properties, free energies

Many Body Perturbation Theory
GW and the Bethe-Salpeter Equation (BSE):
Electronic spectroscopy

Ab initio IR and Raman intensities
Vibrational spectroscopy

MD and Boltzman transport equation
Thermal transport properties

Quantum Espresso & WEST

Y. Ping and D. Rocca and GG Chem. Soc. Rev. 2013

http://eslab.ucdavis.edu/software/qbox/
http://www.quantum-espresso.org/
Computational spectroscopy for realistic systems

New algorithmic developments together with optimized codes and modeling strategies are allowing us to address new problems in materials chemistry and physics.
Computational spectroscopy for realistic systems

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\underline{Vibrational spectroscopy}

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\underline{Thermal transport properties}

\textit{Y.Ping and D.Rocca and Geo Chem. Soc. Rev. 2013}
Photoemission Spectra: Quasi particle energies from MBPT ($G_0W_0$)

\[(T + V_{\text{ext}} + V_H)\psi_n(r) + \int dr' \Sigma(r, r', E_n)\psi_n(r') = E_n\psi_n(r)\]

\[\Sigma(r, r', i\omega) = \frac{1}{2\pi} \int d\omega' G(r, r', i(\omega - \omega')) W(r, r', i\omega')\]

- Self energy expressed in terms of eigenvalues and eigenvectors of the dielectric matrix
- Frequency integration using Lanczos algorithm and contour deformation

**Algorithm enables GW calculations:**
- without explicit calculation of empty single particle orbitals
- without explicit diagonalization and storage of dielectric matrices
- scaling: $N_{\text{eig}}N_{pw}N_v^2$ (instead of $N_{pw}^2N_vN_c$ where $N_c >> N_v$; $N_{pw} >> N_{eig}$)
- numerical accuracy controlled by one single parameter

T.A. Pham, H. V. Nguyen, D. Rocca and GG, Phys. Rev. B 2013
Optical spectra and multi-exciton generations

Optical spectra: absorption coeff. by solving the Bethe-Salpeter Equation (BSE):

— We solve the BSE by using the screened exact exchange self energy in the quantum Liouville equations (1st order perturbation theory)

— We compute the static dielectric screening iteratively, by using an eigenvalue decompositions

Full optical spectrum obtained with a numerical workload comparable to Hartree-Fock calculations

Multi-exciton generation: assume it mostly originates from impact ionization and compute conditional probabilities:

\[ \Gamma_i = 2\pi \sum_f \left| \langle X_i | W | XX_f \rangle \right|^2 \delta(E_i - E_f) \]
Computational spectroscopy for realistic systems

Optical spectra

\[ \text{Si}_{124}\text{H}_{96} \]

\[ \text{WO}_3 \]

Photoemission and band offsets

492 atoms

1560 electrons

85 Ry PW cutoff

592 electrons

No TD approx

D. Rocca, M. Voros, A. Gali & GG, JCTC 2014

M. Govoni & GG 2014 (preprint)

Qbox + QE modules + WEST-parallel

Multi-exciton generation

\[ \Gamma_i = 2\pi \sum_f |\langle X_i | W | X_i \rangle|^2 \delta(E_i - E_f) \]

Y. Ping, D. Rocca, GG, PRB 2013

M. Voros, A. Gali, D. Rocca, GG and G. Zimanyi PRB 2013
**Computational spectroscopy for realistic systems**

*Ab-initio* MD and electronic structure calculations (GGA, VdW and hybrid DFT)

Structural models, trends in electronic properties, free energies

Many Body Perturbation Theory
GW and the Bethe-Salpeter Equation (BSE):
Electronic spectroscopy

**Ab initio IR and Raman intensities**

Vibrational spectroscopy

MD and Boltzmann transport equation
Thermal transport properties

Y. Ping and D. Rocca and *GG Chem. Soc. Rev.* 2013
Fundamental understanding of interfacial electronic properties

- Probe absorption processes and band edges of water and semiconductors and oxide with many body perturbation theory
- Probe interfaces and chemical reactions at interfaces with vibrational spectroscopy

*Y. Nagata et al. JPC-Lett 2013*
Raman spectra obtained from coupled ab initio MD and Density Fcunt. Pert. Theory calculations

- Intensity of Raman spectra from time correlation functions of the polarizability tensor

\[ I_{iso}^{\text{Raman}} \propto \int dt e^{-i\omega t} \langle \bar{\alpha}(0) \bar{\alpha}(t) \rangle \]
\[ I_{aniso}^{\text{Raman}} \propto \int dt e^{-i\omega t} \left\langle \frac{2}{15} \text{Tr}(\beta(0)\beta(t)) \right\rangle \]

\[ \alpha = \bar{\alpha} I + \beta \quad \bar{\alpha} = \text{Tr}(\alpha) / 3 \]

- Polarizability tensor computed within density functional perturbation theory (DFPT)* on ab-initio MD trajectories**

\[ (H_{SCF} - \varepsilon_n) \left| \bar{\psi}_n^{\mu} \right\rangle = -P_c \left[ H_{SCF}, r_\mu \right] |\psi_n\rangle \]
\[ (H_{SCF} - \varepsilon_n) \left| \Delta^E \psi_n \right\rangle = -e \sum_\mu E_\mu \left| \bar{\psi}_n^{\mu} \right\rangle - P_c \Delta V_{lf} \left| \psi_n \right\rangle \]

\[ P^\mu = -\frac{4e}{V} \sum_{n=1}^N \left\langle \bar{\psi}_n^{\mu} \right| \Delta^E \psi_n \left\rangle \]

\[ \alpha^{\mu\nu} = P^\mu / E^\nu \]

Raman spectra obtained from coupled ab initio MD and Density Fcnt. Pert. Theory calculations

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\[ I_{iso}^{Raman} \propto \int dt e^{-i\omega t} \langle \bar{\alpha}(0) \bar{\alpha}(t) \rangle \quad I_{aniso}^{Raman} \propto \int dt e^{-i\omega t} \left( \frac{2}{15} \text{Tr}(\beta(0)\beta(t)) \right) \]

\[ \alpha = \bar{\alpha} I + \beta \quad \bar{\alpha} = \text{Tr}(\alpha) / 3 \]

- Intensity of IR spectra from time correlation functions of molecular dipole

\[ \alpha(\omega) = \frac{2\pi \omega^2 \beta}{3cVn(\omega)} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \langle \sum_{ij} \mu_i(0) \cdot \mu_j(t) \rangle \]

- Sum frequency generation spectra from dipole-polarizability correlations

\[ \chi_{ijk}(\omega) \propto \int dt e^{i\omega t} \langle \alpha_{ij}(0) \mu_k(t) \rangle \]

Computational spectroscopy for realistic systems

New algorithmic developments together with optimized codes and modeling strategies are allowing us to address new problems in materials chemistry and physics
Computational spectroscopy for realistic systems

**Accuracy** of calculations still heavily impacted by underlying DFT description of single particle states
Excited states and transport properties

- Theoretical and computational strategies

- Short stories on solar energy conversion
  - Embedded nanoparticles
  - Si-based clathrates
  - Photo-electrodes for water catalysis
Semiconducting nanostructures for 3rd generation photovoltaics (PV)

• Beyond the Shockley-Queisser limit (33.7% ; ideal p-n junction with 1.34 eV band gap) with a single band gap solar cell

• Avoid converting light into heat → Multi-exciton generation (MEG)
  
  • Quantum confinement “helps” MEG but in “friendly” materials pushes electronic gap beyond solar spectrum
  
  • Charge extraction and transport in nanostructures: difficult to engineer and control
Semiconducting nanostructures for 3rd generation photovoltaics (PV)

- Beyond the Shockley-Queisser limit (33.7% ; ideal p-n junction with 1.34 eV band gap) with a single band gap solar cell
- Avoid converting light into heat → Multi-exciton generation (MEG)

**Problem:** Design realistic models of semiconductor nanostructures exhibiting efficient MEGs and favorable charge extraction and transport mechanisms

- Compute MEG rates from first principles
- Devise models of embedded NPs
- Understand charge transport

A.Nozik et al. Nanolett. 2007
Find Si NPs with ‘solar’ gaps & efficient MEGs

`High pressure Si cores` → lower the gap and increase multi-exciton generation probability

\[ E_n^{qp} = \varepsilon_n + \langle \psi_n | \sum E_n^{qp} | \psi_n \rangle - \langle \psi_n | \hat{V}_{xc} | \psi_n \rangle \]

Find Si NPs with ‘solar’ gaps & efficient MEGs

`High pressure Si cores` → lower the gap and increase multi-exciton generation probability

$\Rightarrow$ BC8 NPs allow for the first time for efficient MEG within the solar spectrum!
BC8 nanoparticles discovered in black Si and synthetized via colloidal route

- Laser induced recoil pressure waves create BC8&R8 Si nanoparticles in a-Si regions within core of nanopillars
  
  M. Smith, E. Mazur et al., J. Appl. Phys. 110, 053524 (2011)

- Colloidal route (reduction of SiI₄ with n-butyllithium, capped with octanol and precipitated from solution)

NPs embedded in solid matrices

Si-I in a-Si  Si-III (BC8) in a-Si

How do we embed nanoparticles?

T.S.Li, F.Gygi and GG, Phys Rev Lett 2011
Joint computational synthesis and characterization from *ab initio* MD

- **Ab initio MD**: Insert Si nanoparticle in crystalline ZnS; amorphize ZnS matrix, remove small Zn clusters
  - S is drawn from the matrix and the Si surface is terminated by sulfur
  - The electronic gap of the NP is substantially lowered
- Engineer S content to form type-II heterojunction
Joint computational synthesis and characterization

- **Computational spectroscopy:**
  - Verify band offsets and band gaps found @PBE level of theory with hybrid functionals * and GW calculations **
  - Analyze localization properties of valence and conduction states and relate them to recombination rates
  - *Surgery to extract NP with relevant shell to compute MEG*

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**Solar nanocomposites with complementary charge extraction pathways for electrons and holes: Si embedded in ZnS**

*S.Wipperman, M.Voros, A.Gali, F.Gygi, G. Zymanyi and GG PRL 2014*
Naturally nanostructured Si

Newly synthesized type I clathrate with low thermal conductivity, good thermal stability and promising thermoelectric properties

Si based clathrates: \( K_8\text{Al}_8\text{Si}_{38} \)

Y. He and GG 2013 Nanolett. 2014

Can it be a good solar material as well?

Y. He, F. Sui, S. Kauzlarich and GG, EES-Comm 2014
Naturally nanostructured Si

Our predictions:

- Quasi direct band gap of ~ 1 eV, tunable in the IR and visible range by strain engineering
- Mobilities much superior to a-Si and 6 to 10 smaller than c-Si
- Holes and electrons localized on different cages

Experiments:

Computed electron mobility: ~49 cm²/V/s at room temperature;

Measured electron mobility by Hall effect: ~39 cm²/V/s
$K_8Al_{8}Si_{38}$ is a promising photovoltaic material

- Small thermal conductivity: $\sim 1.8$ W/mK
- Stable over a wide temperature range: up to 1050 K
- Cheap, Earth abundant elements
- Direct band gap: 0.5~1.4 eV
- Low carrier recombination rate
- High carrier mobilities

Y. He, F. Sui, S. Kauzlarich and GG, EES-Comm 2014
Y. He and GG Nanolett. 2014
Excited states and transport properties

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Search for “good” materials for photoanode and photocathode for water splitting

\[ \text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2(\Delta) + \text{H}_2(\text{g}); \quad \Delta G = +237 \text{ kJ/mol} \]

(1.3 eV/e, \(\lambda_{\text{min}} = 1100 \text{ nm}\))
Ionization potential and electron affinity of liquid water

Liquid water: samples of 512 electrons, generated by “ab-initio” simulations

Beyond DFT: We showed that GW corrections are crucial to obtain band edge positions in good agreement with experiments

Band-edges of functionalized Si surfaces in water

Ab initio MD + band offsets calculations @ G₀W₀ level

- Solid-liquid interaction is not negligible even in the case of hydrophobic surfaces

T.A. Pham, D. Lee, E. Schwegler and G.G. 2014 (preprint)
Hydrophilic surface: multiple effects involved in VBM and CBM shifts

- Water orientation
- Charge transfer
Search for “good” materials for photoanode and photocathode for water splitting

- How can we modify the material’s structure and/or morphology so as to decrease its band gap (~ 2.6 eV) and approach its valence band to the redox of water?

Doped-WO$_3$ and solid solutions
Optimize the band edge position of WO$_3$:

- Different phases of solid WO$_3$
- Intercalation of small molecules (N$_2$) in WO$_3$ lattice
- Solid solutions
Screening materials: Generalized Kohn-Sham Formalism

- Non-local potential
  \[ v^{\text{GKS}}(r, r') = v_H(r) + v_{xc}(r, r') + v_{\text{ext}}(r) \]

- Full & range separated hybrids (RSH)
  \[ v_{xc}(r, r') = \alpha v_{\text{exx}}(r, r') + (1 - \alpha) v_{\text{exx}}(r, r') + \beta v_{\text{SR}}(r, r') + (1 - \beta) v_{\text{SR}}(r) + v_c(r) \]
  for example:
  \[ v_{\text{exx}}^\text{LR}(r, r') = - \sum_{i=1}^{N_{\text{occ}}} \phi_i(r) \phi_i^*(r') \frac{\text{erf}(\omega |r - r'|)}{|r - r'|} \]

<table>
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<tr>
<th>Functional Name</th>
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<th>( \beta )</th>
<th>( \omega )</th>
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Focus on full-range hybrid \( \beta = 0, \omega = \infty \) with one mixing parameter \( \alpha \)
Self-Consistent Hybrid (sc-hybrid)

- A parameter free hybrid density functional for periodic systems
- The fraction of Hartree-Fock exchange ($\alpha$) is determined self-consistently.

$\varepsilon_\infty$ is the static dielectric constant

- No empirical input
- Cost: same order of magnitude as an ordinary hybrid calculation
- Applicable to all condensed phases

Self-Consistent Hybrids (sc-hybrid)

- A wide array of semiconductors and insulators

- CRYSTAL09\textsuperscript{a} electronic structure package
- All-electron calc. except W and Hf (ECPs)
- Basis sets modified from Alhrich’s def2-TZVPP and def2-QZVPP molecular basis
- Polarizabilites evaluated with CPKS\textsuperscript{b} implementation in CRYSTAL09

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{diagram.png}
\caption{Energy gap (E\textsubscript{g}) and dielectric constant (\(\varepsilon_\infty\)) for materials with a self-consistent hybrid (sc-hybrid) approach.}
\end{figure}

Comparison with experiment: dielectric constant

\[ \epsilon_{ij} = \delta_{ij} + \frac{4\pi\varepsilon^2}{V} \chi_{ij} \]

polarizability \( \chi_{ij} \) volume \( V \)

Mean Absolute Errors

- sc-hybrid results in excellent agreement with experimental macroscopic dielectric constants

<table>
<thead>
<tr>
<th></th>
<th>PBE ( \alpha = 0 )</th>
<th>PBE0 ( \alpha = 0.25 )</th>
<th>sc-hybrid ( \alpha = 1/\text{sc-}\varepsilon_{\infty} )</th>
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Comparison with experiment: electronic gaps

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- Similar accuracy as GW for energy gaps

MAE $= 0.46 \pm 0.21$

MARE $= 5.9\% \pm 4.6\%$

Comparison with experiment: electronic gaps

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<th>hybrid $\alpha = 1/\varepsilon_{\infty}$</th>
<th>hybrid $\alpha = 1/\varepsilon_{\infty}$</th>
<th>sc-hybrid $\alpha = 1/sc-\varepsilon_{\infty}$</th>
<th>Exp.</th>
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[Exp. values are typically experimental results for comparison with theoretical calculations.]
Comparison with experiment: bandwidths

- Improved bandwidths
- Improved d band positions
- ZnO: still under-bound, similar to GW calculations

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<th>Exp.</th>
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Summary and Conclusions

- We used computational spectroscopy coupled to ab initio molecular dynamics to predict promising materials for solar energy conversion.

- Several of our predictions were confirmed by experiment.

- We interpreted several experiments on oxides.

Complexity of materials & processes calls for the ability to compute multiple properties.
Many Thanks To My Collaborators

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@ANL, LLNL, NERSC

http://galligroup.uchicago.edu/