“The energy challenge is one of the greatest moral and intellectual imperatives of our age”
Grand Energy Challenge

Gap between production and demand: ~14TW by 2050
Install one 1GW new power plant/day for the next 40 yrs!

<table>
<thead>
<tr>
<th>Energy source</th>
<th>World Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar</td>
<td>36,000 TW</td>
</tr>
<tr>
<td>Geothermal</td>
<td>10 TW</td>
</tr>
<tr>
<td>Biomass</td>
<td>7 TW</td>
</tr>
<tr>
<td>Hydro</td>
<td>5 TW</td>
</tr>
<tr>
<td>Wind</td>
<td>4 TW</td>
</tr>
<tr>
<td>Tide</td>
<td>2 TW</td>
</tr>
</tbody>
</table>
“Progress largely driven empirically, understanding of even existing cells is lacking” – DOE report, 2010

1. Correlated impurities + Coulomb interaction
2. Multiple scattering theory
3. Plasmon-enhanced solar cells
4. Avalanches on driven Bethe-lattices
5. Designing path-breaking PV architectures
6. Strong Coulomb interaction in nanoparticles
Solar Cells Are Extremely Wasteful

1. No absorption below gap: photon wasted
2. Absorption to bottom of conduction band: efficient
3. Absorption high into band: excess energy heats cell

Optimization of gap: max efficiency: 31% (Shockley Queisser 1961)

In real PV cells 80-85% of incident solar energy is lost!
5. Path-breaking PV Designs

Present technology: 31% limit for

- single junction
- one exciton per photon
- relaxation to band edge

E_g

multiple junctions

multiple gaps

extract hot carriers

multiple electrons per photon
6. Strong Coulomb Interaction in Nanoparticle Solar Cells

1. Generate multiple electrons by each photons! How?

2. Increase strength of Coulomb interaction so that $\tau_{x\rightarrow xx} < \tau_{e-ph}$

3. Maximize Coulomb interaction by using nanoparticles with radius less than screening length - Nozik (2001)


Max efficiency for Solar Cells with Multiple Exciton Generation (MEG): 44%
**MEG in Nanoparticle Solar Cells: Basics**

Klimov (2004) pump & probe:
- found new class of excited states, shorter lived than excitons
- identified them as Multi-Exciton states
- reported Quantum Yield (QY=#(electrons)/photon) upto 700%
Bawendi (2008): charging effects can be misinterpreted as MEG

Beard (2011): **MEG is present in NPs after charging is suppressed**
MEG: Consensus Status

* Conversion efficiency good: MEG more efficient in NPs than in bulk, as slope on relative energy scale $h\nu/E_g$ is closer to theoretical max.

* Threshold energy bad: But $E_g$ is larger in NPs, so on absolute energy scale NP solar cells absorb smaller fraction of solar spectrum
The Solar Collaborative at UC Davis

1. **Reduce gap** to maximize benefit of high energy conversion efficiency of MEG-based NP solar cells

2. **Explore MEG in non-toxic materials**
   
   MEG primarily demonstrated with toxic materials:
   
   environmental regulations discourage their use:
   
   concentrate instead on Si, Ge

3. **Optimize quantum confinement**
   
   Competing demands on Quantum Confinement in NPs:
   
   increase confinement to enhance Coulomb and thus MEG
   
   decrease confinement to extract the photo-electrons:
The Solar Collaborative at UC Davis/UCSC

Experiment:
S. Kauzlarich - synthesize NPs
D. Larsen - photoluminescence (PL/TA) characterization of NPs
S. Carter - assemble NPs into working solar cells

Theory:
G. Galli, A. Gali, G. Zimanyi - gap reduction by manipulating NP shape, reconstruction, embedding
M. Voros
Z. Bai, D. Rocca - code development for Bethe-Salpeter
D. Paul - multivariate analysis of PL/TA data
Characterizing Nanoparticle Solar Cells

TEM image of ALD of Cu$_2$S onto TiO$_x$ with radius <1nm

I-V of PbS NP solar cell:
- Large current enhancement at low T!
- Efficiency: 8%
- Role of NP-NP distance?
Theory: Turbo-charged Time-Dependent Density Functional Analysis

1. NP Spectrum - How to decrease gap
   1.1. Effect of surface reconstruction
   1.2. Effect of shape
   1.3. Effect of NP-NP distance

2. Multi-Exciton Generation
   2.1. Screening of interactions
   2.2. Effect of surface reconstruction

3. Code development for Bethe-Salpeter Equation (BSE)
   3.1. Liouvillian super-operator matrix formalism
   3.2. Projecting out unoccupied states
   3.3. Lanczos continued fraction solution of BSE
   3.4. Self-consistent treatment of self-energy \( \text{Im}\Sigma \)
1. NP Spectrum:
1.1. Effect of Surface Reconstruction

Surface reconstruction reduces gap by ~10% and creates intra-gap states

Reducing symmetry of shape reduces gap because a lot of transitions which were forbidden by selection rules become allowed.

Gali, Kaxiras, Zimanyi, Meng, PRB (2011) 15
1. NP Spectrum:
1.3. Effect of NP-NP separation

NP spectrum is impacted at surprisingly large NP-NP separations – QY enhancement at low T?
2. Multi-Exciton Generation:
2.1. Screening of interactions

- static screening approximation
- hydrogenated surface

Energy dependence of screening is minimal:
static approximation is self-consistent

Screening is surprisingly strong even for smallest NPs

- screening is smaller for the smaller NP (~7.5 vs. 12)

static dielectric constant of bulk Si ~12
2. Multi-Exciton Generation:

2.2. Effect of Surface Reconstruction

1. Reconstruction (H64 -> H40):

   MEG creation starts at 30% lower energies because gap reduction

2. Gap reduction:

   Driven by increased density of continuum states, not isolated defect states
3. Code Development for Bethe-Salpeter Equation

3.1. Self-consistent treatment of self energy $\Sigma$

3.2. Liouvillian super-operator formalism:
   eigenvalues of $L$ give excitation energies

3.3. Coulomb Hole + Screened Exchange

3.4. Summation over conduction states avoided by projecting to valence states

3.5. Bethe-Salpeter equation for interactions

3.6. Polarizability determined by Lanczos continued fractions

3.7. Turbocharging by vectorising (~ GPUs for video games)
3. Code Development for Bethe-Salpeter Equation
Comparison to Literature: Si

This work: 12 x 12 x 12+shift k-point mesh


CPC 180, 1392 (2009)
SUMMARY

1. Solar energy problem is intellectually complex and morally honorable
2. Multiple Exciton Generation by strong Coulomb interactions is one of the most promising pathways to increase the solar cell efficiency
3. Energy conversion efficiency by MEG in NPs is better than in bulk
4. NP Gap needs to be reduced: optimizing shape, surface reconstruction, NP-NP distance & surface chemistry are promising
5. Advanced many-body methods (Liouville operators, BSE, SC ImΣ, Lanczos continued fractions) are adapted
6. Optimizing quantum confinement for maximizing MEG vs. extracting photo-electrons efficiently remains central challenge
Memristors – A Revolution on the Horizon

Olle Heinonen (Argonne)
Duk Shin (UC Davis)
GTZ (UC Davis)
Memristors – The excitement

There are two really good computers on Earth: CPUs & Brains
## CPUs vs. Brains

<table>
<thead>
<tr>
<th>Similarity: both are based on switching elements</th>
<th>CPU</th>
<th>Brain</th>
</tr>
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<tbody>
<tr>
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<td>Neuron</td>
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<th>Difference: memory</th>
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<th>Brain</th>
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<th>Difference: number of terminals of switching element</th>
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<td>3 Emitter, collector, gate</td>
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<td>Axon, dendrite</td>
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| Memristors | Similarity: both are based on switching elements | Difference: memory | Difference: number of terminals of switching element |
## CPUs vs. Brains

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<td>2: In &amp; out terminal</td>
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Memristor Manifesto

Until now, a key justification for doing condensed matter physics was to accept the existing design of CPUs, and only to make its elements smaller and faster.

If we can make a switch with a memory, we can give a completely new building block into the hands of computer scientists, forcing them to completely reorganize CPU architecture.
Memristor Manifesto II.

1. 70-80% of CPU cycles used for shuffling data between processor and memory. Transistors with memory allow in-situ processing, integrating logic and storage: no need to shuffle data.

2. In-situ processing allows hierarchically distributed processing by millions of cores in parallel: a revolution in CPU design.

3. In-situ processing can accelerate computation time dramatically.

Secondary:

1. Memristors are a non-volatile memory: flash-beater, much faster access time.

2. Two terminals: qualitatively simpler wiring topologies.

3. A single memristor can perform logical function equivalent to the 6 transistors of an SR latch: much higher element density.
Memristors – The Explosion

HP group of Stan Williams reported hysteretic/switching behavior in Pt/TiO/Pt structures: Nature 2008 May. As of midnight: 401 citations
Performance: HP at the Sweet Spot

1. High endurance:
   - $10^9$ is enough for DRAM replacement
   - $10^{15}$ is needed for processor applications

2. Fast write time: $<10$ nsec
   - beats flash by several orders of magnitude

3. Low energy consumption: 1 pJ/operation

4. Long retention: > 10 years
“4D Scaling” - Crossbar Design

- Simple crossbar: 1 ON memristor shorts row
- Rotate crossbar
- 2D CMOS array used to address blue vias,
  2D CMOS array to address red vias = “4D”
- 3D possible because of 1pJ/operation
Transition Metal Oxides Make Great Memristors

Electrode: Au, Pt

TMO: PrCaMnO, (Ba,Sr)TiO, SrZrO, CeO, NiO, TiO, TaO

IBM-Zurich patent
Mechanism? – Electrons!

- Inhomogeneities are ubiquitous in TMOs: conduction channels are formed during switching.
- Switching: high field drives insulating TMO through Mott transition to become metallic.

Rozenberg 2006-2010

Becker et al PRL ‘02
**Mechanism? – Vacancies!**

Switching = Movement of Oxygen vacancies (HP)

- Cause of switching is ion movement: explains long memory
- Domain wall between high R and low R region moves
- True nano-phenomenon: effect scales with 1/size, absent in macroscopic limit.
Our Simulations

Model:

Electrons:
- Coulomb interaction
- grain charging energy
- disorder
- move driven by electric field to lower energy
- mobility~vacancy density

Vacancies:
- move driven by electric field generated by electrons
- mobility~exponential in field
No hysteresis without vacancy movement

No vacancy movement

Vacancy movement

No hysteresis

Hysteresis

FIG. 6. IV curves with varying disorders
Simulation vs. Experiment

FIG. 6. IV curves with varying disorders

Simulation

Cu/WO3/PT cell
Our Model - Next Generation

- 3000 atoms
- Random energies
- Coulomb interaction (100,000 grid point)
- Electrons jump by master eq.
**HP Phenomenological Simulations**

**HP simulations (Strukov)**

Simulation: \( w(ON) = 0 \)

**ON/OFF width measured**

Expt: \( w(ON) = 1.4 \text{nm} \)
Outstanding Problems

Switching is still ill-understood:

1. Debatable phenomenological assumptions

   \[ \dot{w} = f_{\text{off}} \sin\left( \frac{i}{i_{\text{off}}} \right) \exp \left[ -\exp \left( \frac{w - a_{\text{off}}}{w_c} - \frac{|i|}{b} \right) - \frac{w}{w_c} \right] \]

2. Simulation: \( w(\text{ON})=0 \) vs. Expt: \( w(\text{ON})=1.4\text{nm} \)

3. Presently: large \( V(\text{ON}) \) device-to-device fluctuations
   Uniformity is needed for scaling
   Presently: control/select circuitry is added, losing several advantages
Broad Distribution of Switching Parameters

![Graph showing the distribution of resistances](image_url)

- **Graph a**: Log-log plot of resistance vs. cycles, showing a broad distribution of switching parameters.
- **Graph b**: Histograms of ON resistance ($R_{ON}$) with relative frequency, indicating a log-normal distribution.

**Note**: The specific values and units are not provided in the image. Further analysis would be required to provide precise details.
Summary

1. Memristors are switches with non-volatile memory
2. Distributed processing integrated with memory possible
3. High endurance, fast switching, low power
4. Two-terminals: crossbar architecture
5. Low power: 3(4)D scaling of crossbar layers