Ab-initio studies of optical excitations in solids and molecules

With:
Grigory Kolesov, Dmitry Vinichenko, George Tritsaris, Weili Wang,
Physics Dept., Applied Physics-SEAS, Harvard
Jierong Cheng, Hossein Mosallaei
Electrical Eng., Northeastern U.

(earlier work: Sheng Meng, Jun Ren, Inst. of Phys., Ch. Acad. Sci.)

Sabanci University – May 8, 2014
The need for alternative energy sources

Global carbon dioxide emissions from human activities, 1750-2004

Million metric tons of carbon

Global Temperatures

<table>
<thead>
<tr>
<th></th>
<th>Annual Average</th>
<th>Five Year Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1860</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1870</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1880</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1890</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1910</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1920</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1930</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1940</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1960</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1970</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1980</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1990</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Positive proof of global warming.

In the winter, Georgia is now hospitable to plants like firebush.

Serviceberries and dogwoods can be planted in Nebraska.

A warmer New York helps a type of fungus harmful to Canadian hemlock.

In Seattle, it is more difficult to grow black-eyed susans.

http://www.celsias.com/2007/03/20/channel-4-distances-itself-from-global-warming-documentary/
The challenge of sustainable energy

Report of Intergovernmental Panel on Climate Change

Time and resources running out
The dye-sensitized (3rd generation) solar cell

The Principle: Separate light-absorption and charge collection processes
The Problem:

- Materials for carrier transport with large band gaps

$\text{TiO}_2$ gap = 3.2 eV (200 nm < $\lambda$ < 400 nm)

Light absorption by hybrid cells
The dye-sensitized solar cell (DSSC)

Major issues:
- stability
- efficiency
  Incident Photon to Current Efficiency

$\text{IPCE}(\lambda) = \text{LHE}(\lambda) \times \Phi(\text{inj}) \times \eta(c)$

$\text{LHE} = \text{Light Harvesting Efficiency}$
$\Phi(\text{inj}) = \text{electron injection efficiency}$
$\eta(c) = \text{charge collection efficiency}$
Conventional p-n junction cell (inorganic)
Complex device, simple physics

Copper-Indium-Gallium-Selenide cell

Bulk semiconductor (inorganic)
- delocalized states (band structure)
- nearly free electrons
- single band-gap
Main issue: coupled electron-ion dynamics

Previous work:
- Schroedinger eq. with model Hamiltonian
  Thoss, Miller, Stock, JCP (2000);
  Rego & Batista, JACS (2003);…
- semiempirical Hamiltonian (tight-binding)
  Allen et al., JMO (2003);…
- ground state DFT + TDDFT
  Prezhdo et al., PRL (2005); JACS (2007)…

self-consistent TDDFT with atomic motion

\[ i\hbar \frac{\partial \phi_j(r, t)}{\partial t} = \left[ -\frac{\hbar^2}{2m} \nabla_r^2 + v_{ext}(r, t) + \int \frac{\rho(r', t)}{|r - r'|} dr' - \sum_I \frac{Z_I}{|r - R_I^d|} + v_{xc}[\rho](r, t) \right] \phi_j(r, t) \]

\[ M_J \frac{d^2 R_j^d(t)}{dt^2} = -\nabla_{R_j^d} \left[ V_{ext}(R_j^d, t) - \int \frac{Z_J \rho(r, t)}{|R_j^d - r|} dr + \sum_{I \neq J} \frac{Z_J Z_I}{|R_j^d - R_I^d|} \right] \]

Transport: $10^{-12}$ s

Propagation of electrons in time (TDSE) + Ehrenfest dynamics for ions
Density Functional Theory

Many-body:

$$\left( \hat{H} - E \right) \psi (r_1 \sigma_1, r_2, \sigma_2, \ldots) = 0 \quad : \text{Unsolvable}$$

Hohenberg & Kohn (PRB, 1964):
$$E \left[ V(r) \right] = \min_{\rho(r)} E' \left[ V(r); \rho(r) \right]$$

Kohn & Sham (PRB, 1965):
$$E' \left[ V(r); \rho(r) \right] =$$
$$T_s[\rho] + E_{\text{Hart}}[\rho] + \int \rho(r)V(r)dr + E_{xc}[\rho]$$

$$\left( \hat{H}_{\text{KS}} - \epsilon_i \right) \psi_i(r) = 0$$

W. Kohn, J. Pople
Nobel Prize in Chemistry, 1998

Runge-Gross theorem for TD-DFT
Self-consistent \( e \) propagation

Ionic motion

Check for break down
\[ t_n = n \Delta t; \quad R_n, v_n, \phi_j(t_n), \rho_n = \sum_j |\phi_j(t_n)|^2, \quad \mathcal{H}[R_n, \rho_n] \]

\[
k = 0
\tilde{\phi}_j^0(t_{n+1}) = \exp (-i \hbar \Delta t \mathcal{H}[R_n, \rho_n]) \phi_j(t_n)
\tilde{\rho}_n^0 = \sum_j |\tilde{\phi}_j^0(t_{n+1})|^2
\]

\[
k = k + 1
\tilde{\phi}_j^k(t_{n+1}) = \exp (-i \hbar \Delta t \mathcal{H}[R_n, \tilde{\rho}_n^{k-1}]) \phi_j(t_n)
\tilde{\rho}_n^k = \sum_j |\tilde{\phi}_j^k(t_{n+1})|^2
\]

[Decision diamond]

\[ |\tilde{\rho}_n^k - \tilde{\rho}_n^{k-1}| < \varepsilon ? \]

No
\[ \tilde{\rho}_n^k = \alpha \tilde{\rho}_n^k + (1 - \alpha) \tilde{\rho}_n^{k-1} \]

Yes
\[ \phi_j(t_{n+1}) = \tilde{\phi}_j^k(t_{n+1}), \quad \rho_{n+1} = \tilde{\rho}_n^k \]
Ionic motion

\[ F_{n+1} = -\nabla_{\mathbf{R}} V[\mathbf{R}_n, \rho_{n+1}] \]

\[ \mathbf{R}_{n+1} = \mathbf{R}_n + \mathbf{v}_n \Delta t + F_n (\Delta t)^2 / (2M) \]

\[ \mathbf{v}_{n+1} = \mathbf{v}_n + (F_n + F_{n+1}) \Delta t / (2M) \]

\[ E_{ij} = \langle \phi_i(t_{n+1}) | \mathcal{H}[\mathbf{R}_{n+1}, \rho_{n+1}] | \phi_j(t_{n+1}) \rangle \]

\[ E_{ij} \text{ too large?} \]

- No: \( n = n + 1 \)
- Yes: Decay path
Nano-size: helps in many aspects (e.g. efficiency, transparency, transport, ...)

Approximately complete surface coverage (i.e. densest possible packing of dye molecules)

100 nm

$\text{TiO}_2$

~20 nm sized faceted anatase nanoparticles

Approximately complete surface coverage (i.e. densest possible packing of dye molecules)
Electron and hole motion in DSSC
Charge injection dynamics:

\[ \chi = \int dr |\tilde{\psi}(r)|^2, \quad \tilde{\psi}(r) = \sum_{j \in \text{TiO}_2} c_j \phi_j(r), \]

Injected Electrons \((e)\)

Fit: \(t_0 = 32\) fs, \(t_1 = 40\) fs

Expt.\(^a\): <100 fs

T = 350 K
\(\delta t = 0.02419\) fs
Importance of coupled e-ion dynamics

![Graph showing dynamic and static ions over time](image)

- Dynamic ions
- Static ions

Injected Electrons (e) vs Time (fs)
Relation between electron-phonon motion

Energy Level (eV)

Time (fs)

Bond Length (Ångstrom)

Time (fs)

O-Ti

C-O
D-π-A Dye System Containing Cyano-Benzoic Acid as Anchoring Group for Dye-Sensitized Solar Cells
Masataka Katono, Takeru Bessho, Sheng Meng, Robin Humphry-Baker, Guido Rothenberger, Shaik M. Zakeeruddin, Efthimios Kaxiras, and Michael Gratzel
Langmuir 2011, 27, 14248–14252

84% Incident Photon to Current Efficiency, 3.3% Electric Power Conversion Efficiency
Photocatalytic water splitting system utilizing Pt/TiO$_2$/IrO$_2$: TiO$_2$ is light absorber, Pt is the hydrogen evolution catalyst, and IrO$_2$ is the oxygen evolution catalyst. (P. Kamat, U. Notre Dame)

H$_2$ production from organic molecules using TiO$_2$ nano-particles as photocatalysts (Argonne National Lab)
Example: ozone photolysis

• Excitation HOMO to LUMO: slow dissociation

• Excitation HOMO to LUMO+1: quick dissociation

1\textsuperscript{st} excited state trajectory

- GPAW computation time: 37 days (4 cores)
- TDAP: 1 hour
- Time step: 5 attosec (both)
2nd excited state trajectory
2nd excited state trajectory

• Movie: o3split.mov
• Formaldehyde was photochemically produced from methoxy on TiO$_2$ (110) surface

TDDFT trajectory

• Movie:
  mxssplit.mpg
Manipulating the properties of graphene

Graphene

- Quasi-2D crystal: strongest material recorded $E=1$ TP
- High mobility: as high as $2 \times 10^5$ cm$^2$V$^{-1}$s$^{-1}$
- Low spin-orbit coupling and hyperfine interaction (1% C$^{13}$)
- Unique band structure: massless quasi-particle
- Other properties: room temperature quantum hall effect, Klein paradox, etc.
Proposal for a graphene-based plasmonic device

F4-TCNQ (blue area) and TCNQ+TTF (green area). Projected DOS shows effects of doping and the added molecular DOS signature to the total DOS due to the molecule-graphene interactions.
Properties of copper (fluoro-) phthalocyanine layers deposited on epitaxial graphene

Ren, Sheng Meng, Yi-Lin Wang, Xu-Cun Ma, Qi-Kun Xue, and Efthimios Kaxiras

JOURNAL OF CHEMICAL PHYSICS 134, 194706 (2011)
Spatially resolved dielectric function

(a) Im(\varepsilon) vs. Frequency (THz)
- Green: with F4-TCNQ
- Blue: with TCNQ+TTF

(b) Frequency (THz) vs. \kappa_y (\mu \text{m}^{-1})
- Green: with F4-TCNQ
- Blue: with TCNQ+TTF
- Orange dashed: gold-air
- Orange: gold-SiO_2
Refractive indices of metamaterials made of: (a) patterned graphene, (b) a gold film on top of Gradient Refractive Index dielectric substrate.

[dots: full-wave FDTD simulation; lines: EMT with filling factor (FF) ranging from 0.0 to 1.0]
Waves propagate through the lens region (box) and turn into PW's.
An atomic-scale chisel for sculpting graphene

By Wei Li Wang
Expts. carried out at LBNL’s NCEM
Raw STEM image | Reconstructed image | Ball-and-stick model

(a) 

(b)
Simulation of C atom removal from G with and without Si impurities.
Summary: by combining
- fundamental physics (TDSE)
- methodologies for extending time-scale
- computational tools
   can address complex phenomena of
   intrinsic interest and potential for useful
   applications.