Efficient ab-initio approaches towards the photochemistry of functional molecules on metal surfaces

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Theoretical Chemistry, Technical University Munich

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Motivation

Binary Computer Logic ⇒ The field-effect-transistor
Gate Voltage controls **ON** and **OFF** state

*concept*  
*conception*

*demonstration*  
*demonstrative*

22 nm FinFET

Lilienfeld, 1926  
Heil, 1934

Atalla and Dawon Kahng  
Bell Labs, 1959

Intel  
IEDM, 2012

Lundstrom, www.nanohub.org
Motivation

Moore’s Law

\[ L = 5 \text{ nm} \]

Nano-electronics

\[ L = 5000 \text{ nm} \]

Micro-electronics

http://en.wikipedia.org/wiki/Moore%27s_law

Lundstrom, www.nanohub.org
Motivation

Moore’s Law

$L = 5$ nm

Nano-electronics

$\approx 50$ Ångstrom

Micro-electronics

http://en.wikipedia.org/wiki/Moore%27s_law

Lundstrom, www.nanohub.org

Link: The scale of the Universe
Molecular Nanotechnology $\Rightarrow$ Single Molecules are basic units
Motivation

Molecular Nanotechnology $\Rightarrow$ Single Molecules are basic units

Molecular Switches

Azobenzene

N=N

$hv$, $k_B T$

N=N
Molecular Nanotechnology $\Rightarrow$ Single Molecules are basic units

Molecular Switches
+ Contact

ON
Motivation

Molecular Nanotechnology $\Rightarrow\Rightarrow$ Single Molecules are basic units

Molecular Switches
+ Contact

OFF

Azobenzene

Support/Contact
Motivation

Light- or Electron-triggered Molecular Switching

Comstock et al., PRL 99 (2007), 038301.

Ferri et al., Angew. Chem. 47 (2008), 3407.

Information Storage  Logics  Surface Functionalization
Motivation

**Design Problems**

- Loss of Function
- Insufficient Understanding

**Ferri et al.**, *Angew. Chem.* 47 (2008), 3407.

**Comstock et al.**, *PRL* 99 (2007), 038301.

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**trans-Ab**

<table>
<thead>
<tr>
<th>Quenching excited states</th>
<th>Strong coupling</th>
<th>Steric hindrance</th>
</tr>
</thead>
</table>

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**Ferri et al.**, *Angew. Chem.* 47 (2008), 3407.
Our Goal

⇒ Understanding adsorbate function ⇐

- Accurate description of structure and energetics
- Identify parameters that govern molecular function
- Propose design strategies
- Unraveling transient photodynamics

1. Substrate variation
2. Adsorbate design
3. Coverage
4. Coadsorption
Our Goal

⇒ Understanding adsorbate function ⇐

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Full Dynamical Description of Molecular Switching
Exited State Energetics
Efficient Excited State Methodology
Groundstate Energetics
Adsorbate Structure
Our Approach

Large-Scale Density-Functional Theory Simulations using Castep

Exchange-Correlation Functional Approx.

- Local Density Approx. (LDA)
- Generalized Gradient Approx. (GGA), ...

Problems:

- Self-Interaction Errors
- Neglect of Van-der-Waals interactions

Our Approach

Large-Scale Density-Functional Theory Simulations using CASTEP

$E_{\text{DFT}}^{\text{GS}}[\rho] = T_s[\rho] + \int dr^3 v^\text{ext}(r)\rho(r) + \frac{1}{2} \int \int dr^3 dr' \frac{\rho(r)\rho(r')}{|r-r'|} + E_x^c[\rho] + E_{\text{vdw}}^{\text{surf}}$

$E_{\text{vdw}}^{\text{surf}} = \sum_A \sum_B f(r_{\text{cut}}, A, B) \frac{C_{6}^{AB}}{r_{AB}^6}$

$f(r_{\text{cut}}, A, B) \ldots$ damping function

$C_{6}^{AB} \ldots$ vdW coefficients generated from ab-initio polarizability and dielectric function of solid

1) periodic boundary conditions
2) semi-local XC
3) ultrasoft pseudopotential plane waves (USPP)
4) van-der-Waals correction, DFT+vdw$^{\text{surf}}$


McNellis et al., PRB 80 (2009), 205414.
Our Approach

Large-Scale Density-Functional Theory Simulations using CASTEP

- 1000s of electrons
- $10^6$ plane waves
- different levels of parallelization
  1) high comm. for matrix diagonalization
  2) minimal comm. over Brillouin zone sampling

CASTEP

vdw$^{surf}$


McNellis et al., PRB 80 (2009), 205414.
Adsorbate Structure
### Adsorbate Structure

<table>
<thead>
<tr>
<th></th>
<th>$z$ (Å)</th>
<th>$\omega$ (°)</th>
<th>$\beta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>low cov.</td>
<td>2.61</td>
<td>4.5</td>
<td>-2.0</td>
</tr>
<tr>
<td>($T = 0$ K)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>high cov.</td>
<td>2.81</td>
<td>11.7</td>
<td>15.4</td>
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<td>($T = 0$ K)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>exp.</td>
<td>2.97</td>
<td>-0.7</td>
<td>17.7</td>
</tr>
<tr>
<td>($T = 210$ K)</td>
<td>±0.05</td>
<td>±2.3</td>
<td>±2.7</td>
</tr>
</tbody>
</table>

Collaboration with Prof. Stefan Tautz, FZ Jülich

Comparison to X-Ray Standing Wave experiments

**Mercurio, Maurer, et al., PRB, 88 (2013), 035421.**
Adsorbate Structure

Collaboration with Prof. Stefan Tautz, FZ Jülich
Comparison to X-Ray Standing Wave experiments
Mercurio, Maurer, et al., PRB, 88 (2013), 035421.
Molecule Bistability

![Graph showing relative energy vs dihedral rotational angle]

Molecule Bistability

Molecule Bistability

Molecule Bistability

Groundstate Bistability is lost $\rightarrow$ cis-Ab not stable

Molecule Functionalization

Molecule Functionalization

Molecule Functionalization

Spacer groups → no effect on stability

?excited state mechanism?

STM

STM

STM

STM


Reinhard Maurer

SuperMUC Workshop, Garching
Excited State Method

Efficient Excited State Methodology - \( \Delta \text{SCF} \)?

\( \Delta \text{SCF} \) DFT

Accuracy

MBPT
TDDFT

Speed

Gas phase molecular orbital
\[
\sum_i f_i |\psi_i><\psi_i| + f_c |\psi_c><\psi_c|\]

Reinhard Maurer, PCCP 111 (2010), 6404-6412.
Excited State Method

Efficient Excited State Methodology - $\Delta$SCF ?

McNellis et al., PCCP 111 (2010), 6404-6412.
Excited State Method

Efficient Excited State Methodology - \( \Delta \text{SCF} \)?

MCNELLIS et al., PCCP 111 (2010), 6404-6412.

\[
\Delta \text{SCF} \text{ DFT}
\]

Reinhard Maurer  
SuperMUC Workshop, Garching  
8 / 12
Efficient Excited State Methodology - $\Delta$SCF?

$E_{ex} = E(e^- \uparrow) - E(groundstate)$

Constraining occupation of molecular states

McNellis et al., PCCP 111 (2010), 6404-6412.

Gunnarsson, Lundqvist, PRB 13 (1976), 4274–4298.
Excited State Method

Efficient Excited State Methodology - $\Delta$SCF?

Constraining occupation of molecular states
- Molecular states on the surface?

$E_{ex} = E(e^- \uparrow) - E(groundstate)$

+ Speed of a DFT calculation
- Can only handle excitations with single particle character
- Accuracy?!

Gunnarsson, Lundqvist, PRB 13 (1976), 4274–4298.
Maurer and Reuter, JCP 135 (2011), 224303.
Excited State Method

Efficient Excited State Methodology - $\Delta$SCF?

$E_{ex} = E(e^- \uparrow) - E(\text{groundstate})$

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Maurer and Reuter, JCP 135 (2011), 224303.
Excited State Method

Efficient Excited State Methodology - leΔSCF !

\[ |\psi_c > = \sum_i |\psi_i > < \psi_i | \phi_c > \]

\[ \rho = \sum_i f_i |\psi_i > < \psi_i | + f_c |\psi_c > < \psi_c | \]

\[ \phi_c \quad \ldots \quad \text{Gasphase molecular orbital} \]

\[ \sum_i f_i + \sum_c f_c = N_e \]

- Gavnholt et al., PRB 78 (2008), 075441.
- Maurer and Reuter, JCP 139 (2013), 014708.
Excited State Method - $\text{le}\Delta\text{SCF}$

Maurer and Reuter, JCP 139 (2013), 014708.
Excited State Method - leΔSCF

Maurer and Reuter, JCP 139 (2013), 014708.
Excited State Method - le∆SCF

le∆SCF
Orbital relaxation

hν

correctly describes state shifts and image charge effects

Orbital relaxation ⇒ allows to treat neutral excitations (n/π → π∗) and 'charged' excitations (metal → π∗)

separated systems:

le∆SCF = ∆SCF!

Maurer and Reuter, JCP 139 (2013), 014708.
Excited State Method - leΔSCF

leΔSCF

Orbital relaxation

\[ h\nu \]

\[ \Rightarrow \quad E_{ex} \]

Maurer and Reuter, JCP 139 (2013), 014708.
Excited State Method - $\text{le}\Delta SCF$

$\text{le}\Delta SCF$

Orbital relaxation

$\hbar\nu$

allows to treat

neutral excitations ($n/\pi \rightarrow \pi^*$)

'charged' excitations (metal $\rightarrow \pi^*$)

Maurer and Reuter, JCP 139 (2013), 014708.
Excited State Method - leÅSCF

Excited State Method - leÅSCF

Orbital relaxation

\[ \text{Excited state } \rightarrow \text{Orbital relaxation} \]

\[ \text{correctly describes state shifts and image charge effects} \]

Orbital relaxation allows to treat neutral excitations (n/\(\pi\) \(\rightarrow\) \(\pi^*\)) and 'charged' excitations (metal \(\rightarrow\) \(\pi^*\)).

Maurer and Reuter, JCP 139 (2013), 014708.
Excited State Method - le\(\Delta\)SCF

- Correctly describes state shifts and image charge effects.

- Allows to treat neutral excitations \((n/\pi \rightarrow \pi^*)\) and 'charged' excitations \((\text{metal} \rightarrow \pi^*)\).

Maurer and Reuter, JCP 139 (2013), 014708.
Excited State Method - leΔSCF

Excited State Energetics - First Hints

? Shallow PESs $\rightarrow$ Enough $E_{\text{kin}}$ collected in $\sim 40$ fs ?
Excited State Method - $\text{le}\Delta\text{SCF}$

Excited State Energetics - First Hints

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! $\rightarrow$ Dynamics simulations required !
Explicit Dynamics Simulations

- Reduced Dimensionality
- Efficient Optimizations
- Coupling Models
- Quantum Dynamics
- Analytical Representations
Reduced Dimensionality

Explicit Dynamics Simulations
Explicit Dynamics Simulations

Efficient Optimizations

- Preoptimizations:
  - Force-Fields, Tight-Binding

- Increasing Efficiency:
  - vdW Embedding

Masters Thesis: Georg Michelitsch
Explicit Dynamics Simulations

Analytical Representations

- Many-Body-Expansion / Sparse Grids

\[ V(x) = V^{(0)} + \sum_{i}^{N} V^{(1)}_{i}(x) + \sum_{i,j > i}^{N,N} V^{(2)}_{ij}(x^i, x^j) + \ldots \]

Strobusch, Scheurer, JCP, 140, 074111 (2014)
Explicit Dynamics Simulations

Analytical Representations

- Many-Body-Expansion / Sparse Grids

\[ V(\mathbf{x}) = V^{(0)} + \sum_{i}^{N} V_{i}^{(1)}(\mathbf{x}) + \sum_{i,j>i}^{N,N} V_{ij}^{(2)}(\mathbf{x}^i, \mathbf{x}^j) + \ldots \]

Strobusch, Scheurer, JCP, 140, 074111 (2014)
Adsorbate Photodynamics simulations need to

- be efficient
- be in adiabatic representation
- account for non-adiabatic transitions
- work with simple coupling schemes
- be compatible with friction models
Quantum Dynamics

Adsorbate Photodynamics simulations need to:
- be efficient
- be in adiabatic representation
- account for non-adiabatic transitions
- work with simple coupling schemes
- be compatible with friction models

⇒ Trajectory-Surface Hopping (TSH)
⇒ Independent-Electron TSH

Tully, JCP, 93, 1061 (1990); Shenvi, Roy, Tully, JCP, 130, 174107 (2009)
Explicit Dynamics Simulations

Coupling Models

Need to account for

Non-Adiabatic Coupling between
  - explicitly treated states
  - adsorbate and substrate states

Energy Dissipation due to
  - molecular degrees of freedom
  - substrate phonons and excitons
Conclusions and Outlook

We have....

- ...established an efficient technique to simulate structure, energetics, photoresponse of adsorbed molecular switches
- ...identified reason for switching/non-switching on metal surfaces
- ...analyzed different parameters that control the function

We currently / We will...

- ...investigate the excited state topology and mechanism
- ...perform explicit dynamical simulation of photoswitching

Mercurio, Maurer, et al., PRB, 88 (2013), 035421.
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Thank you for your attention!

Many Thanks to SuperMUC and Team!

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