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

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Motivation

Binary Computer Logic ⇒ The field-effect-transistor

Gate Voltage controls ON and OFF state

concept

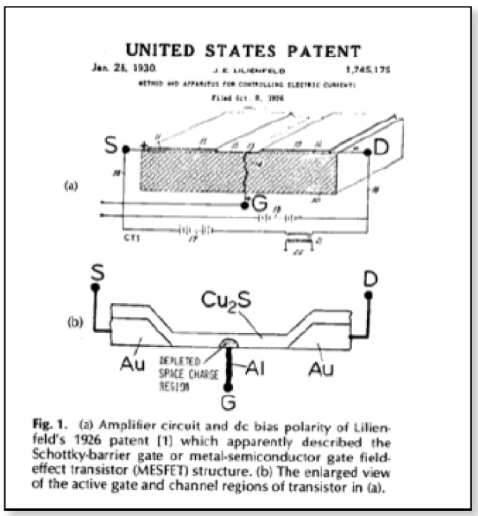
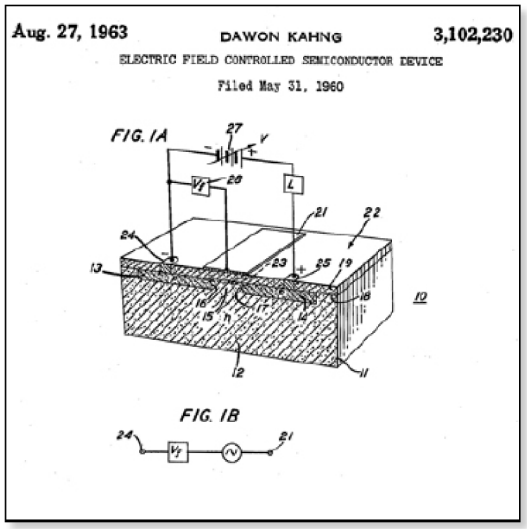


Fig. 1. (a) Amplifier circuit and dc bias polarity of Lilienfeld's 1926 patent [1] which apparently described the Schottky-barrier gate or metal-semiconductor gate field-effect transistor (MESFET) structure. (b) The enlarged view of the active gate and channel regions of transistor in (a).

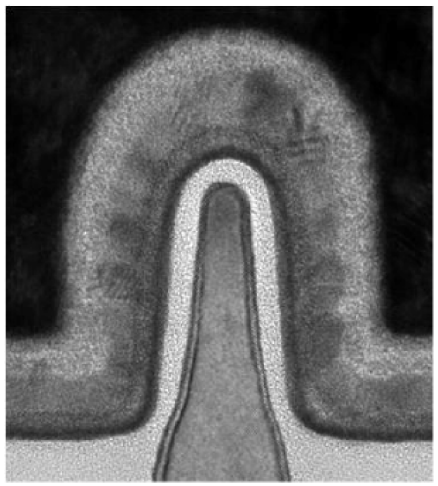
Lilienfeld, 1926
Heil, 1934

demonstration



Atalla and Dawon Kahng
Bell Labs, 1959

22 nm FinFET



Intel
IEDM, 2012

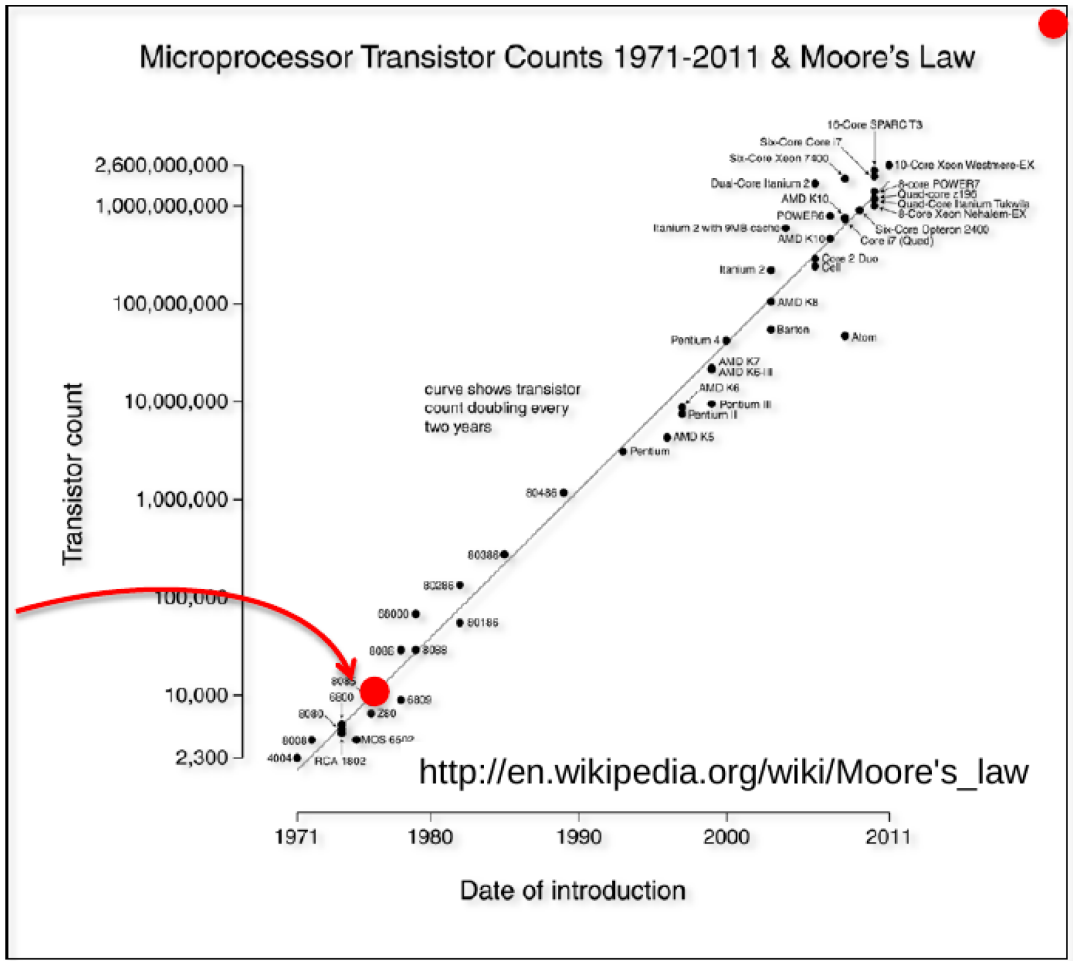
Lundstrom, www.nanohub.org

Motivation

Moore's Law

$L = 5000$ nm

Micro-electronics



$L = 5$ nm

Nano-electronics

Lundstrom, www.nanohub.org

Motivation

Moore's Law

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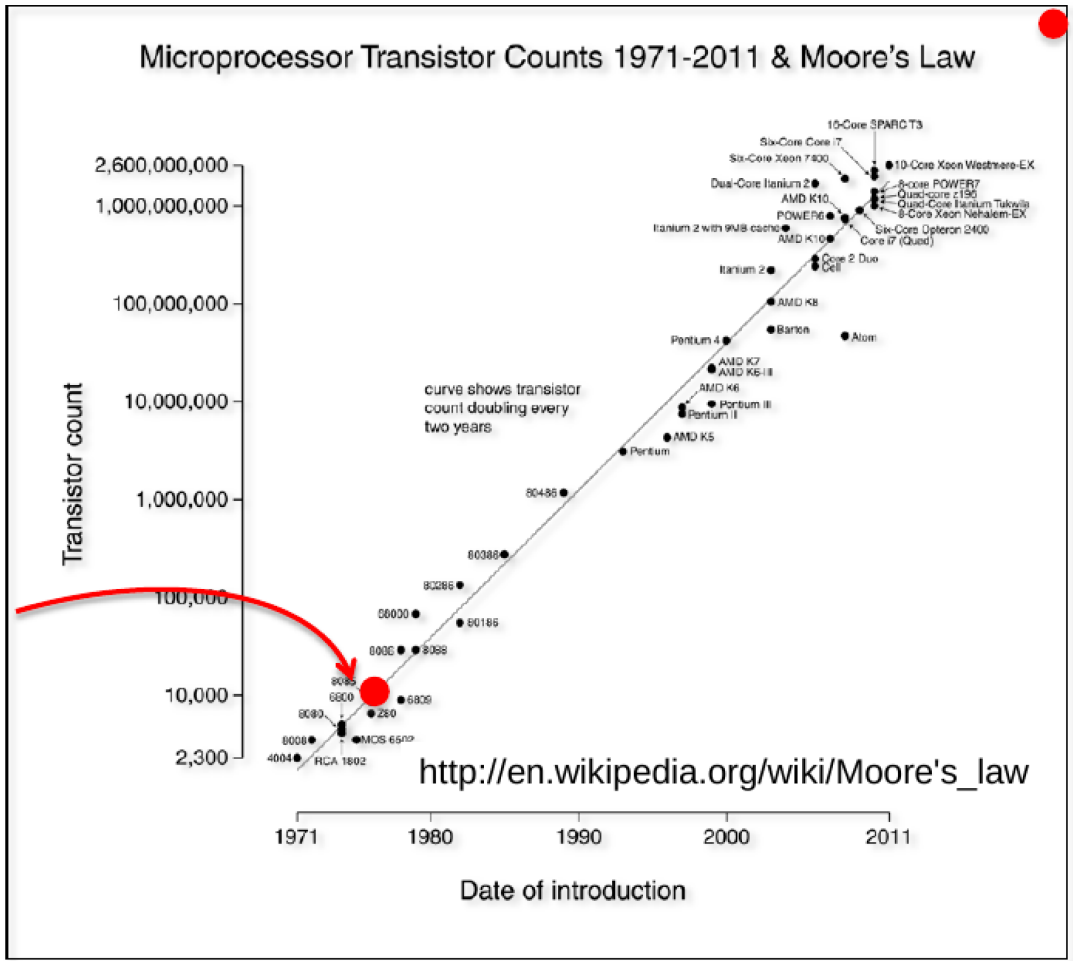


$L = 5$ nm

Nano-electronics

$\approx$ 50 Ångstrom

Lundstrom, www.nanohub.org

Link: The scale of the Universe

Motivation

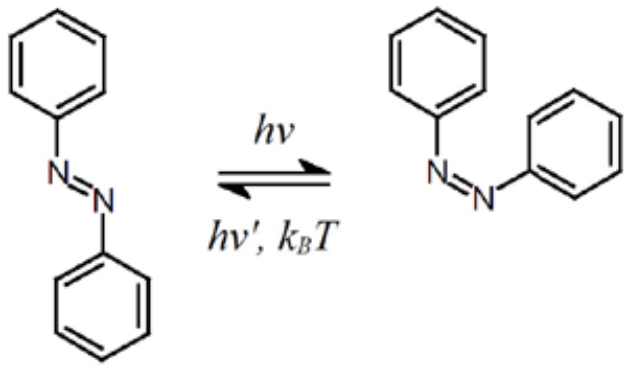
Molecular Nanotechnology $\Rightarrow\Rightarrow$ Single Molecules are basic units

Motivation

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

Molecular Switches

Azobenzene



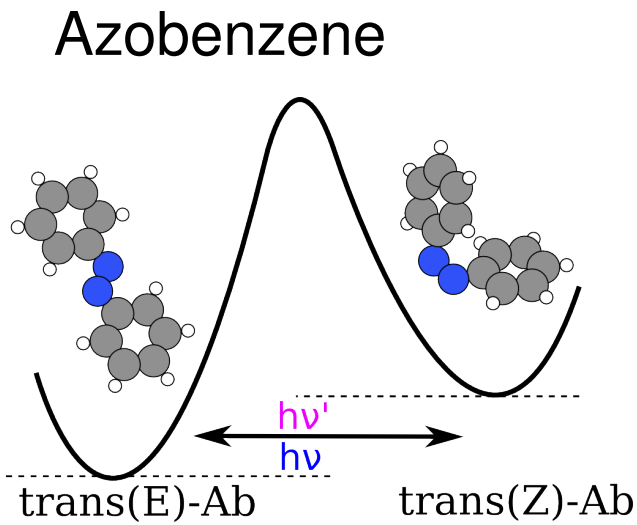
Motivation

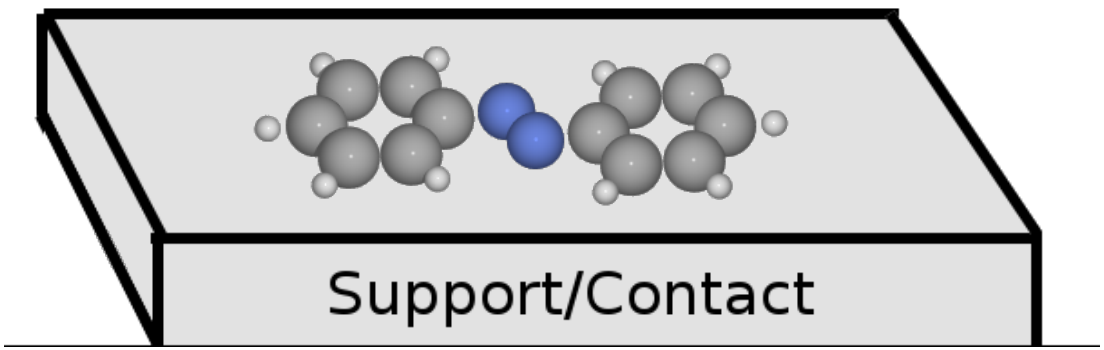
Molecular Nanotechnology ⇒⇒ Single Molecules are basic units

Molecular Switches

+Contact

ON





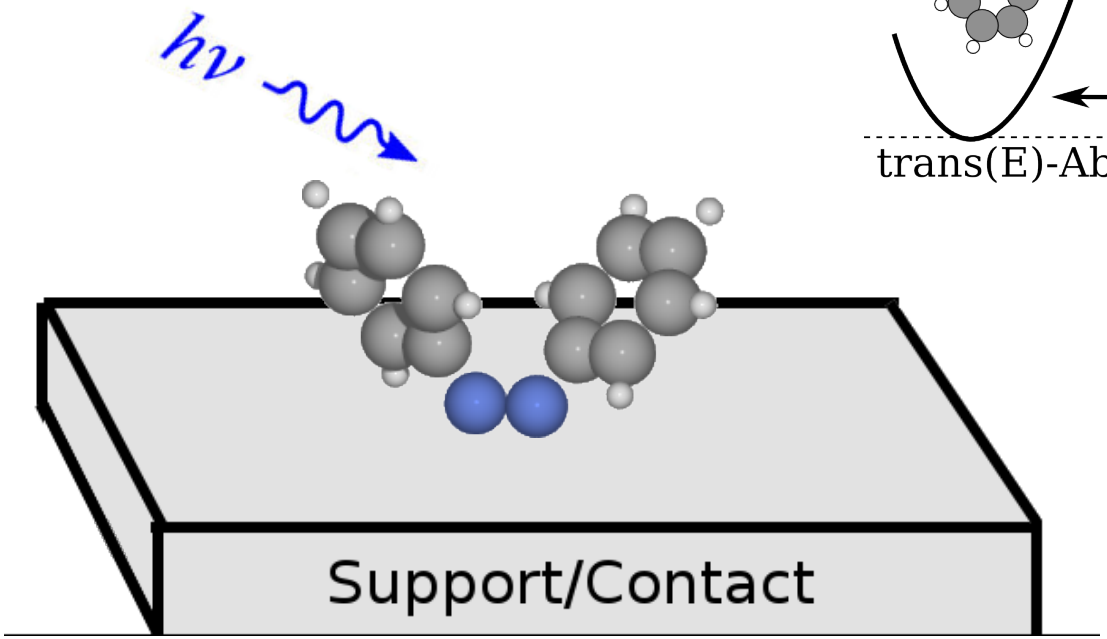
Motivation

Molecular Nanotechnology ⇒⇒ Single Molecules are basic units

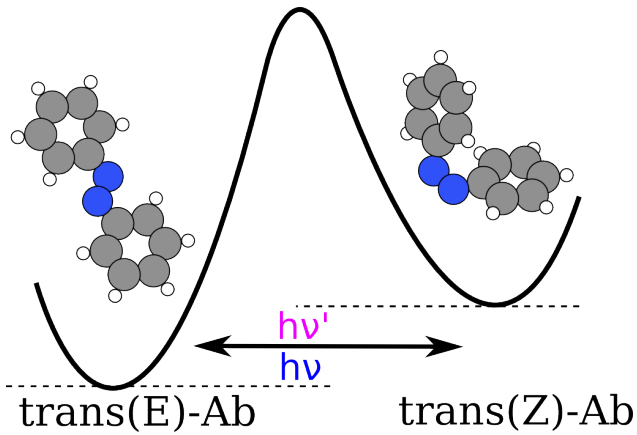
Molecular Switches

+Contact

OFF

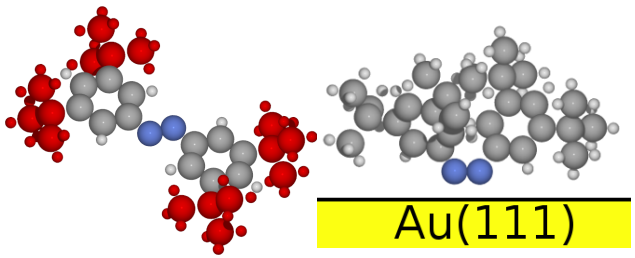


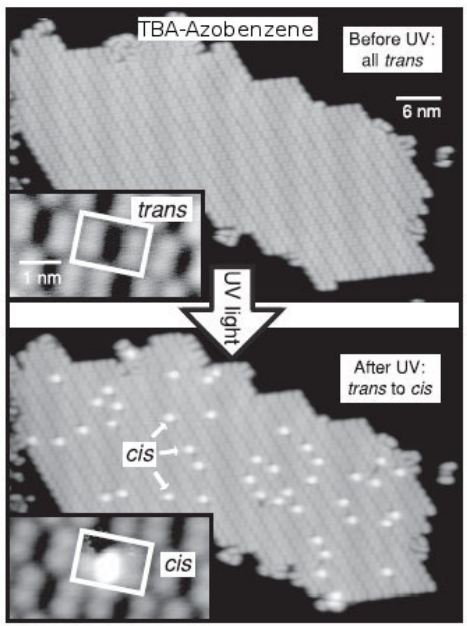
Azobenzene



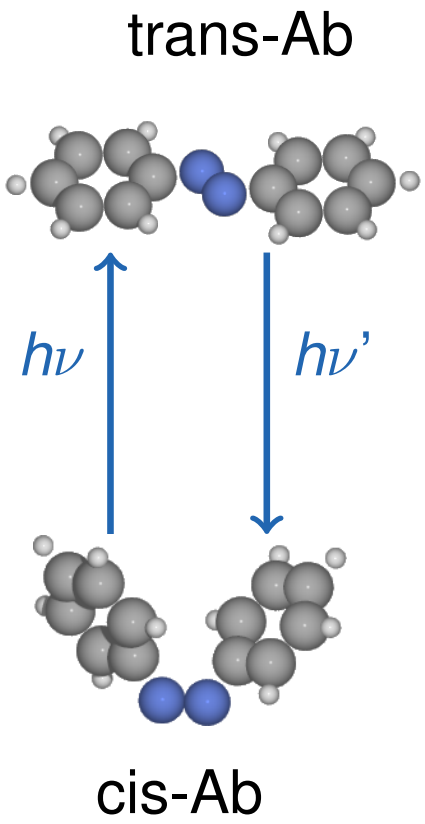
Motivation

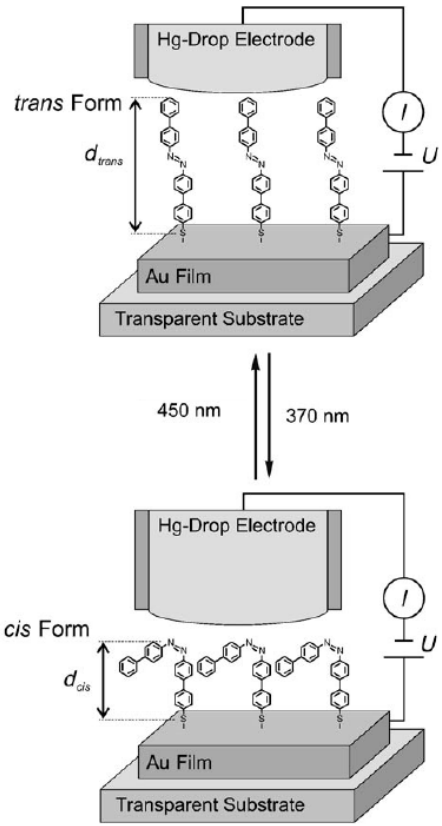
Light- or Electron-triggered Molecular Switching





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



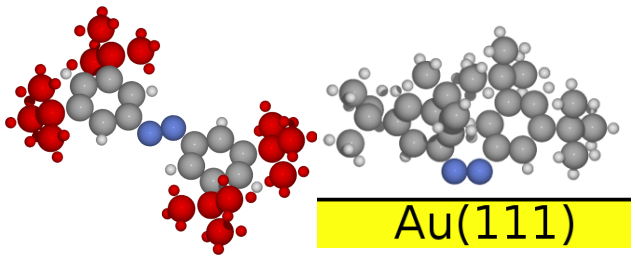


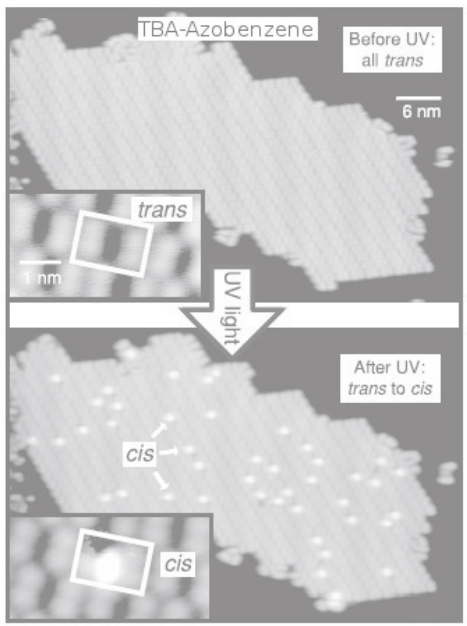
Ferri *et al.*, Angew. Chem. 47 (2008), 3407.

Information Storage | Logics | Surface Functionalization

Motivation

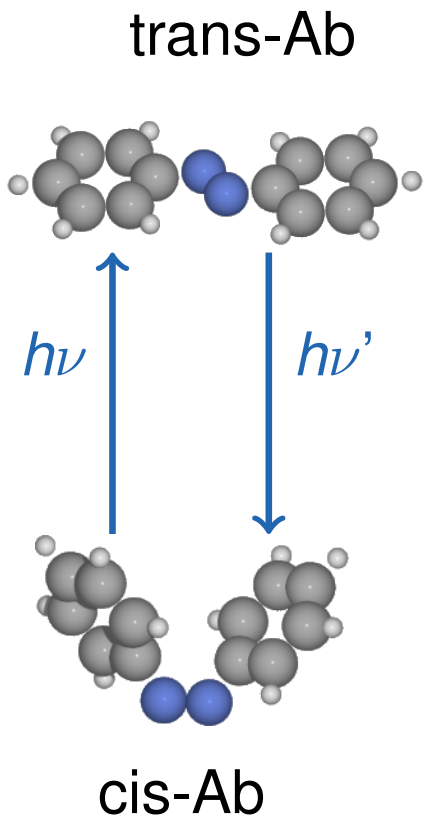
Design Problems



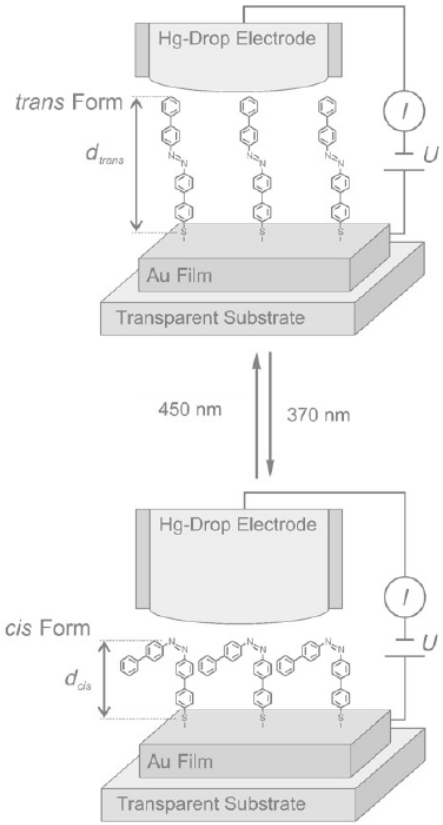


Comstock *et al.*, PRL 99 (2007), 038301.

Loss of Function



Insufficient Understanding



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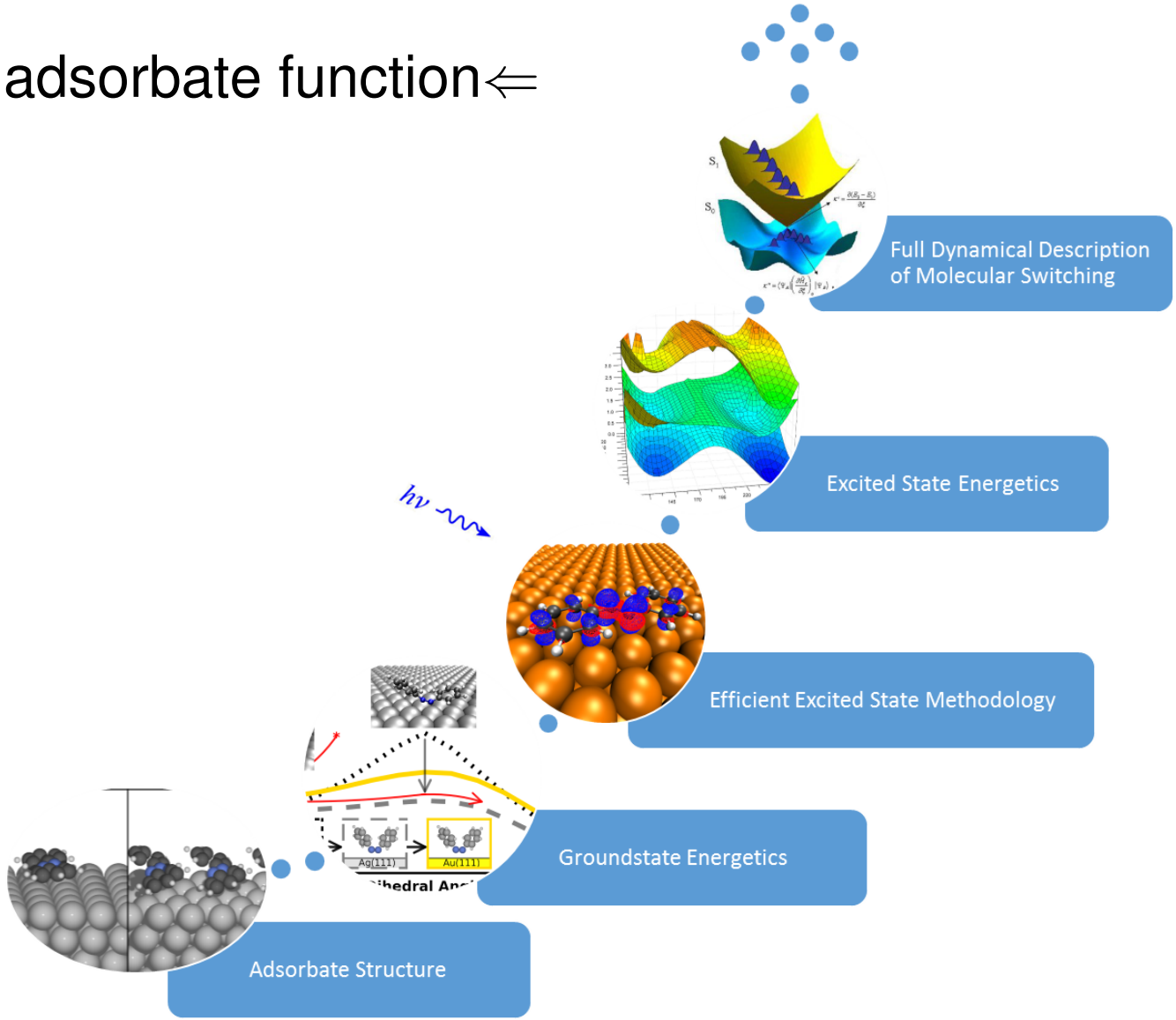
Quenching excited states

Strong coupling

Steric hindrance

Our Goal

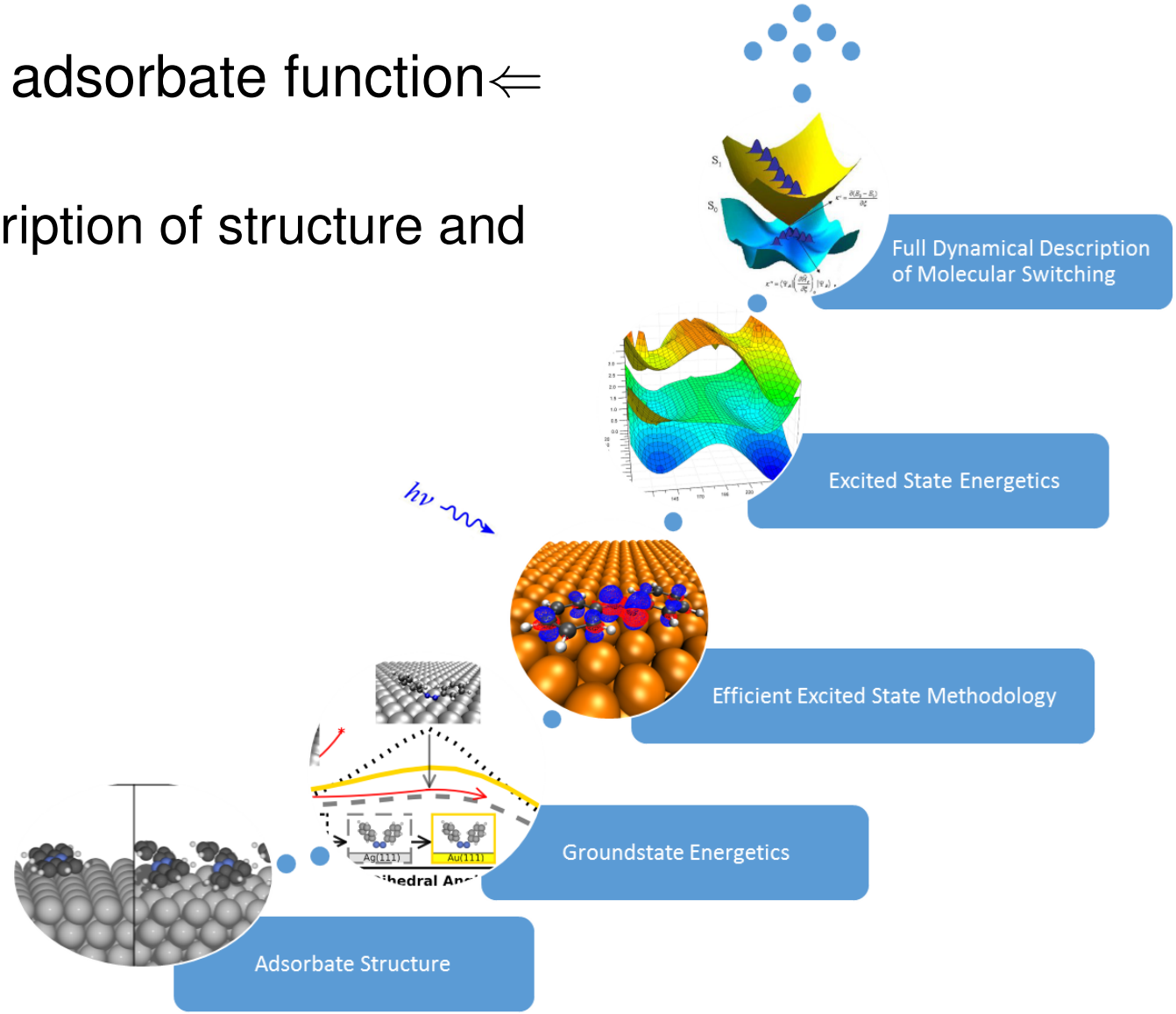
⇒Understanding adsorbate function⇐



Our Goal

⇒Understanding adsorbate function⇐

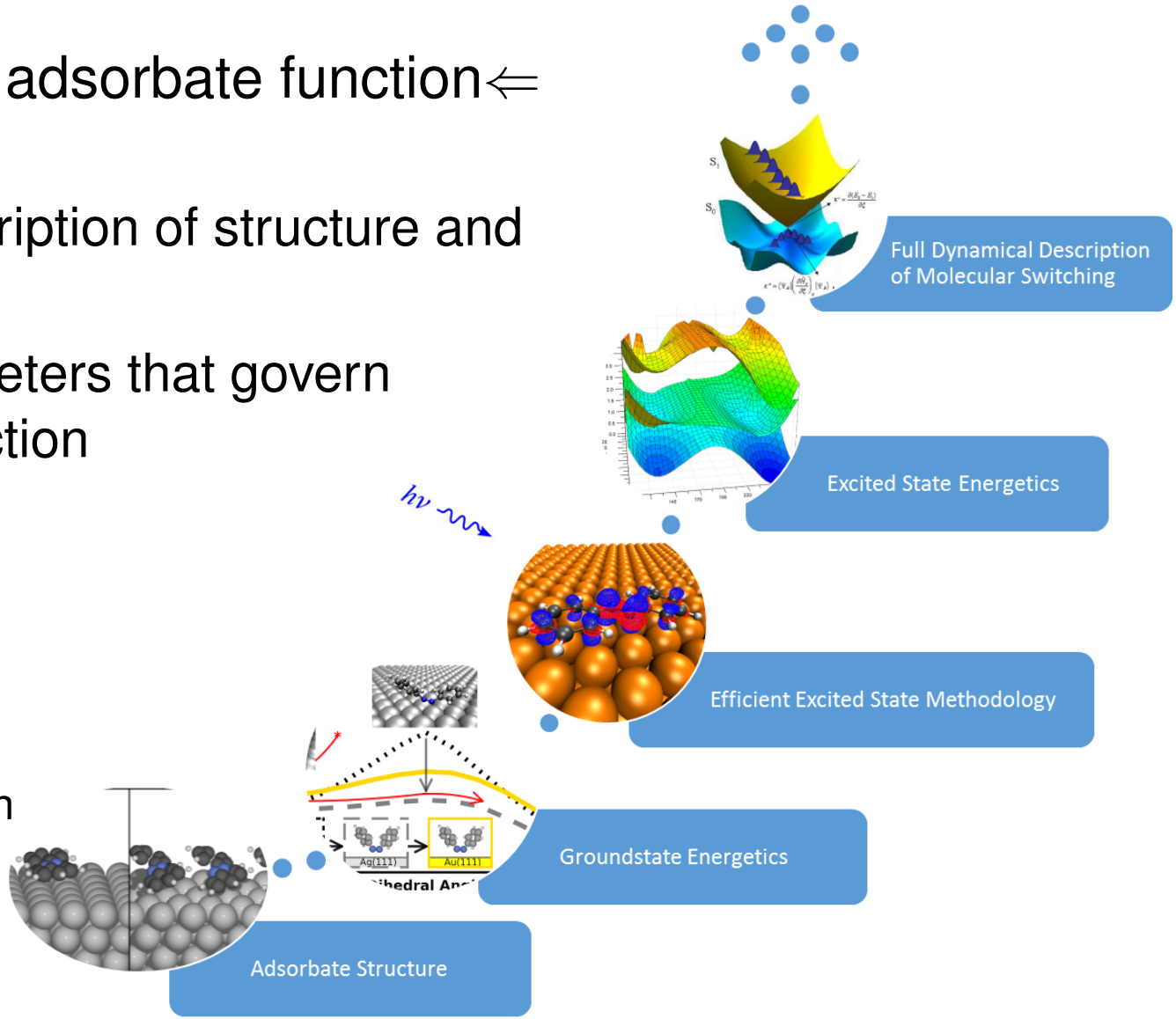
- Accurate description of structure and energetics



Our Goal

⇒Understanding adsorbate function⇐

- Accurate description of structure and energetics
- Identify parameters that govern molecular function



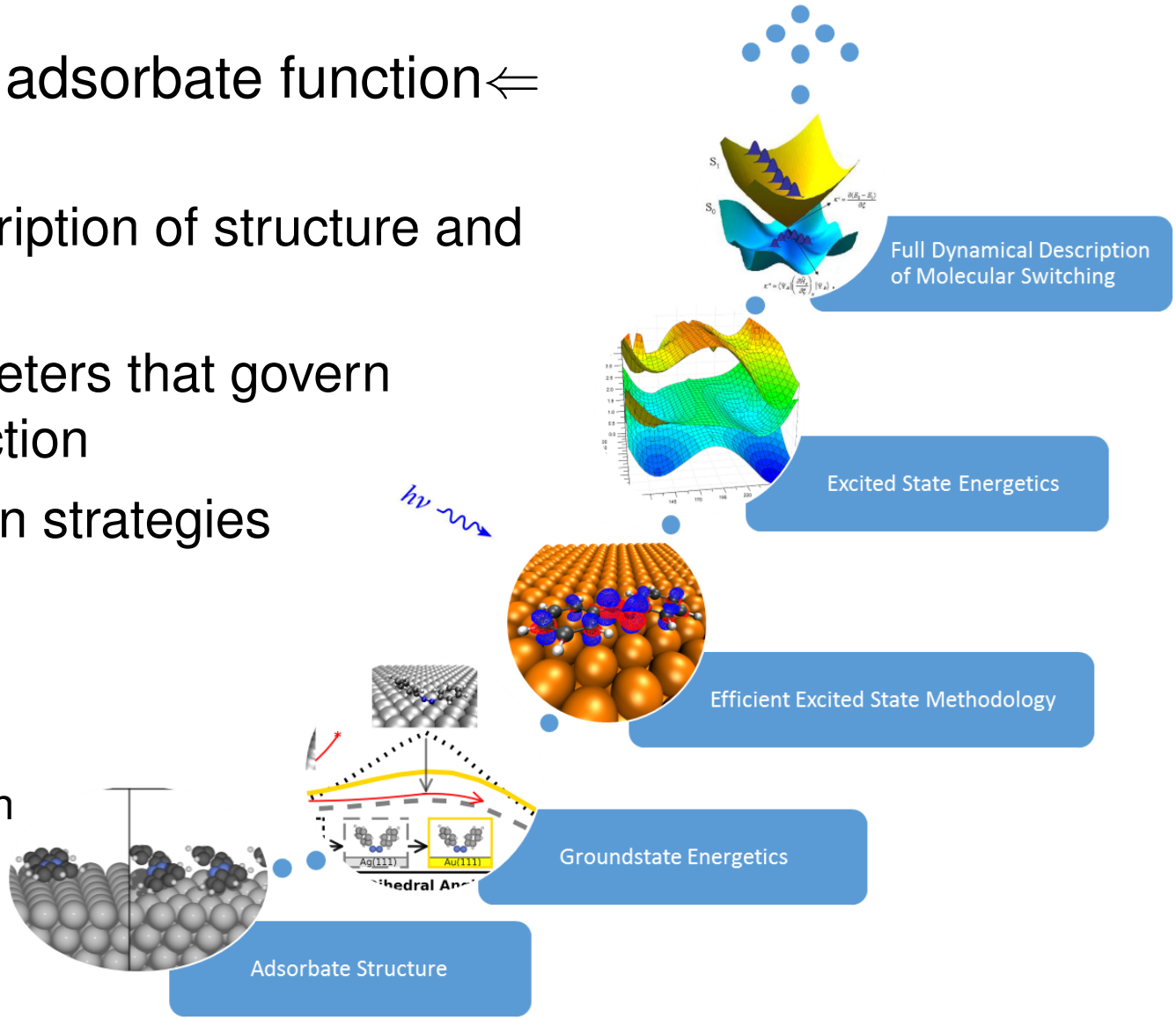
Parameters:

1. substrate variation
2. adsorbate design
3. coverage
4. coadsorption

Our Goal

⇒Understanding adsorbate function⇐

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



Parameters:

1. substrate variation
2. adsorbate design
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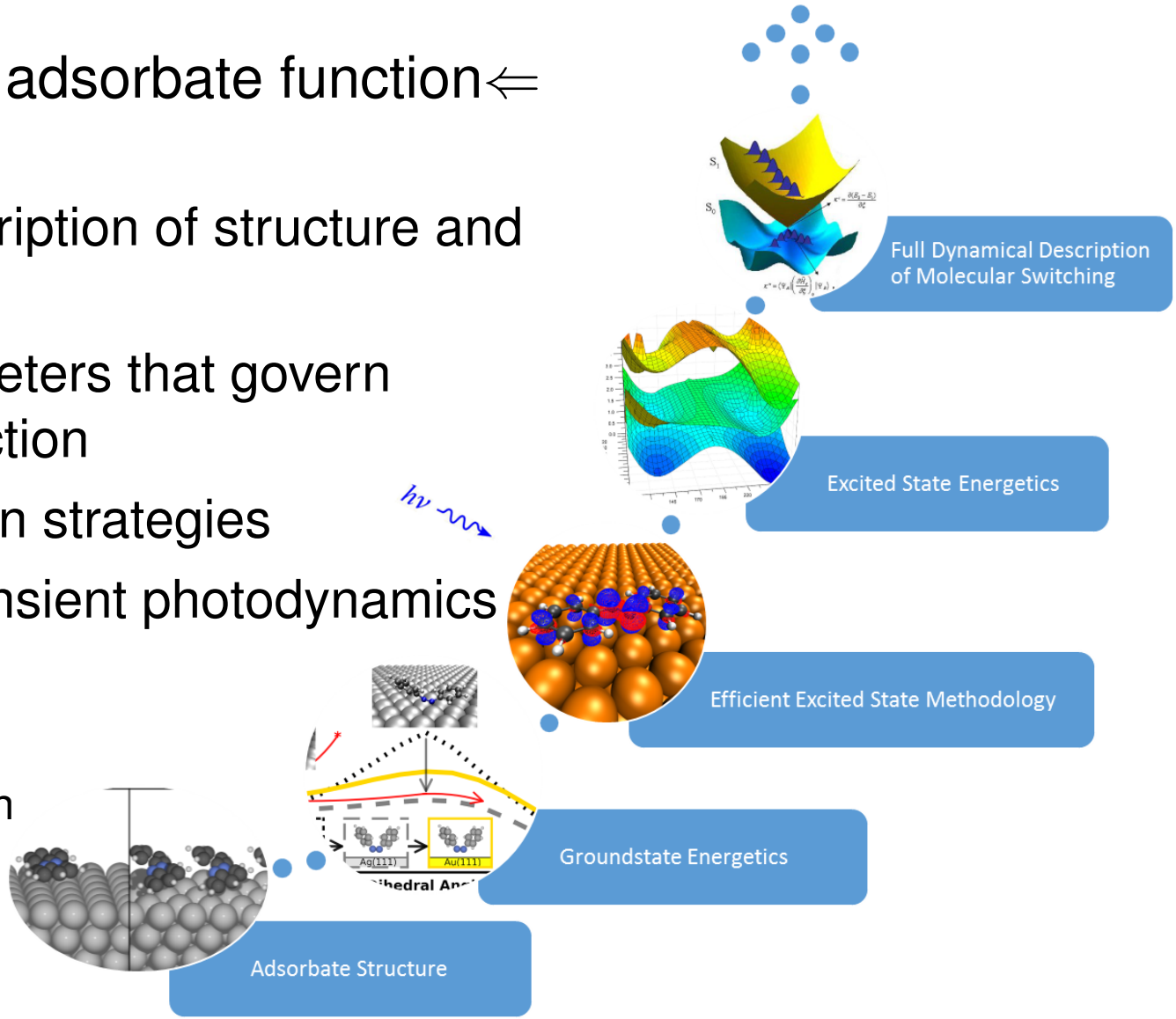
Our Goal

⇒Understanding adsorbate function⇐

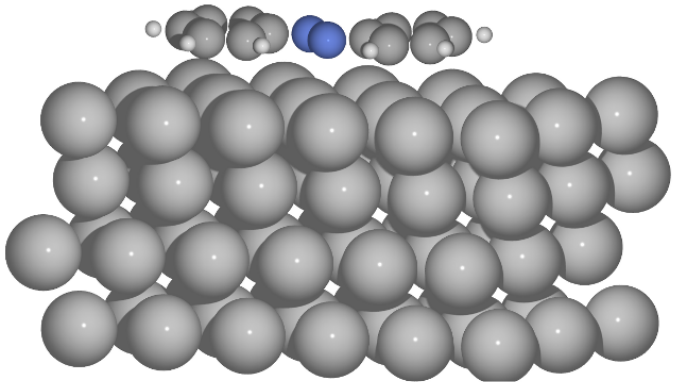
- Accurate description of structure and energetics
- Identify parameters that govern molecular function
- Propose design strategies
- Unraveling transient photodynamics

Parameters:

1. substrate variation
2. adsorbate design
3. coverage
4. coadsorption



Our Approach



Large-Scale
Density-Functional Theory
Simulations using CASTEP

$$E_{\mathrm{GS}}^{\mathrm{DFT}}[\rho] = T_s[\rho] + \int dr^3 v^{\mathrm{ext}}(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2}\int\int dr^3 dr^3 \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E^{xc}[\rho]$$

Exchange-Correlation Functional Approx.

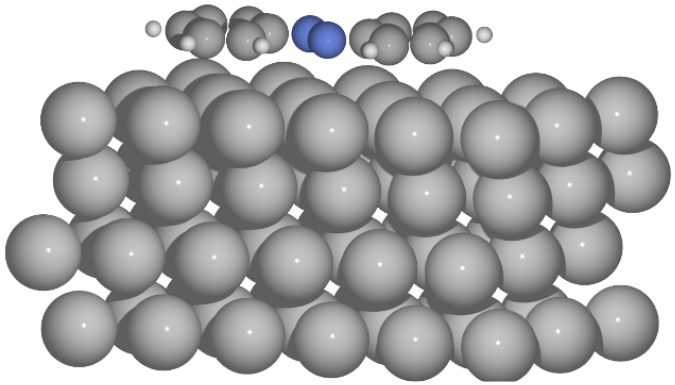
- Local Density Approx. (LDA)
- Generalized Gradient Approx. (GGA), ...

Problems:

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

CASTEP Segall, *et al.*, J. Phys.: Cond. Matt. **14** (2002), 2717.

Our Approach



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$$E_{\mathrm{vdw}}^{\mathrm{surf}} = \sum_A \sum_B f(r_{\mathrm{cut}}, A, B) \frac{C_6^{AB}}{r_{AB}^6}$$

$f(r_{\mathrm{cut}}, A, B)$ . . . damping function

C_6^{AB} . . . vdW coefficients generated from ab-initio polarizability and dielectric function of solid

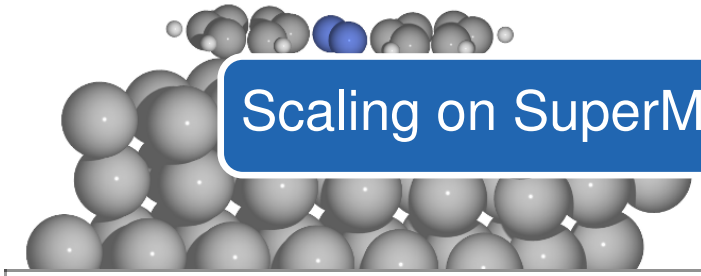
1) periodic boundary conditions
2) semi-local XC
3) ultrasoft pseudopotential plane waves (USPP)
4) van-der-Waals correction, DFT+vdw$^{\mathrm{surf}}$

CASTEP Segall, *et al.*, J. Phys.: Cond. Matt. **14** (2002), 2717.

vdw$^{\mathrm{surf}}$ Ruiz, *et al.*, PRL **108** (2012), 146103.

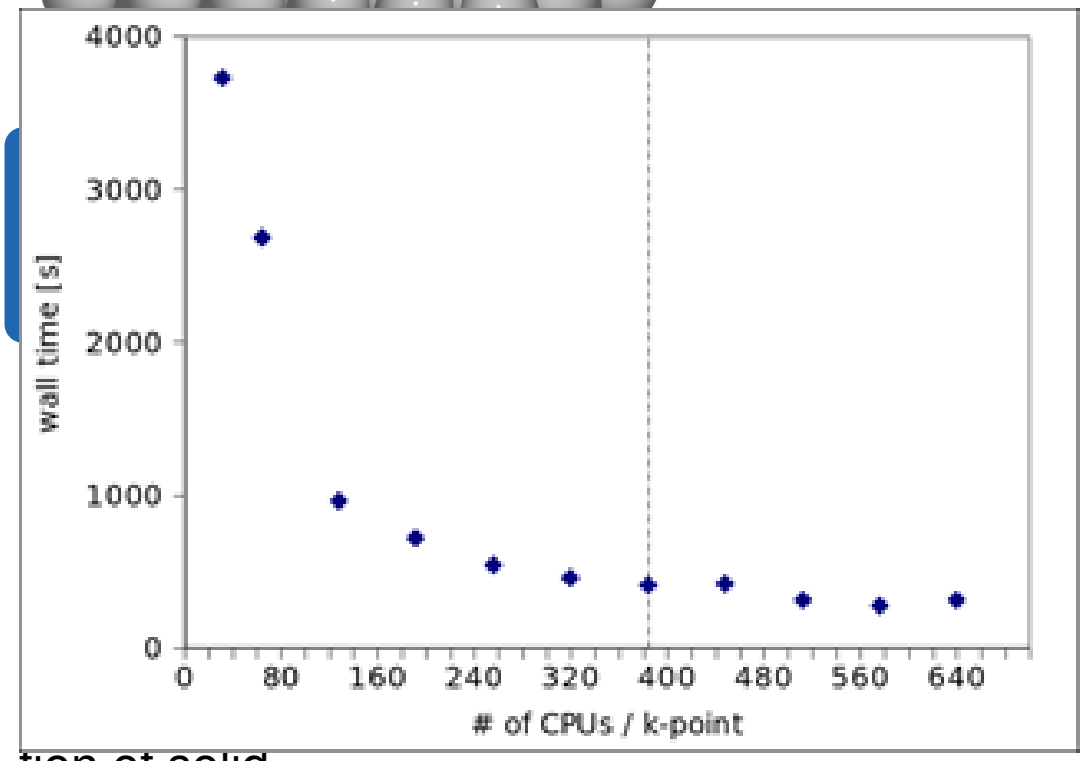
McNellis *et al.*, PRB **80** (2009), 205414.

Our Approach



Scaling on SuperMUC

Large-Scale
nsity-Functional Theory
Simulations using CASTEP



tion of solid

- 1000s of electrons
- 10^6 plane waves
- different levels of parallelization

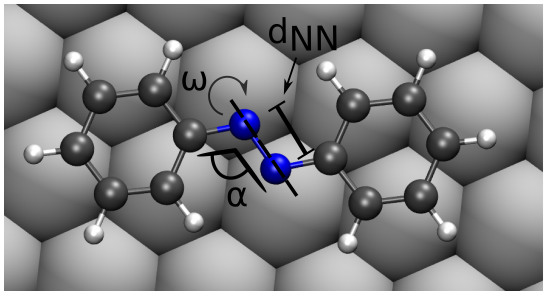
1) high comm. for matrix diagonalization
2) minimal comm. over Brillouin zone sampling

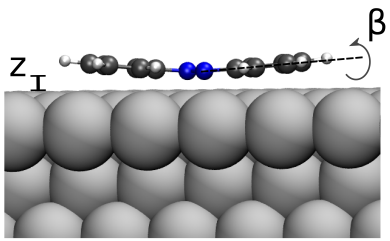
CASTEP Segall, *et al.*, J. Phys.: Cond. Matt. **14** (2002), 2717.

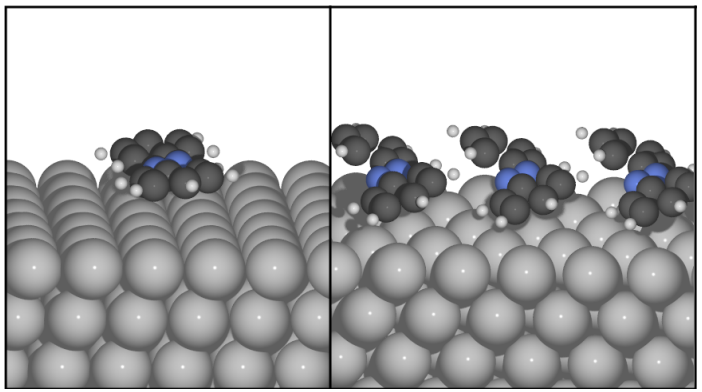
vdw^{surf} Ruiz, *et al.*, PRL **108** (2012), 146103.

McNellis *et al.*, PRB **80** (2009), 205414.

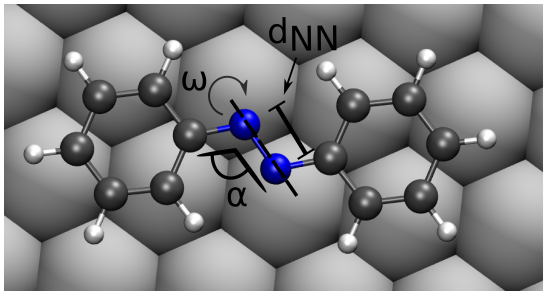
Adsorbate Structure

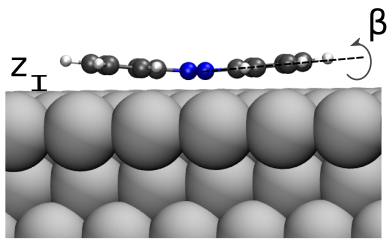


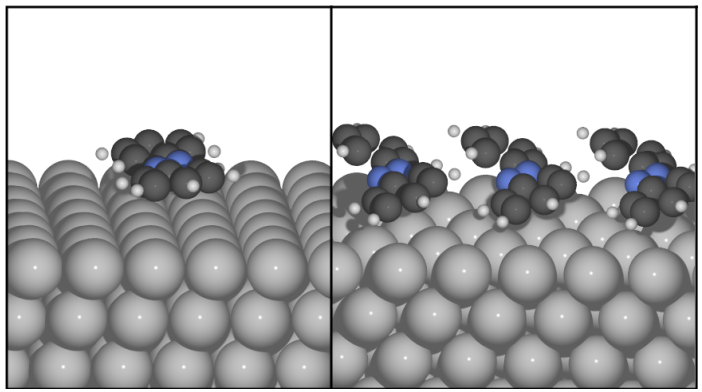




Adsorbate Structure







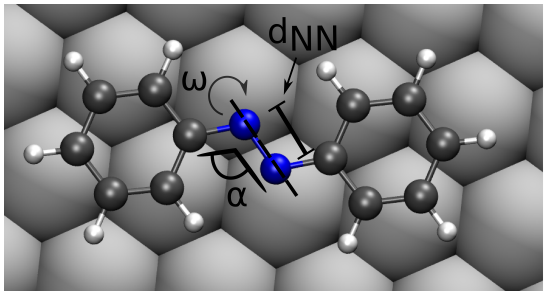
	z (Å)	ω (°)	β (°)
low cov. ($T = 0\ K$)	2.61	4.5	−2.0
high cov. ($T = 0\ K$)	2.81	11.7	15.4
exp. ($T = 210\ K$)	2.97 ±0.05	−0.7 ±2.3	17.7 ±2.7

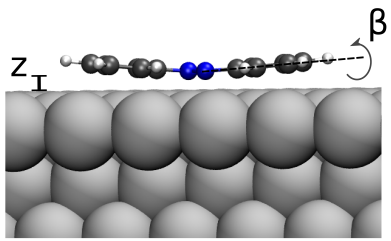
Collaboration with Prof. Stefan Tautz, FZ Jülich

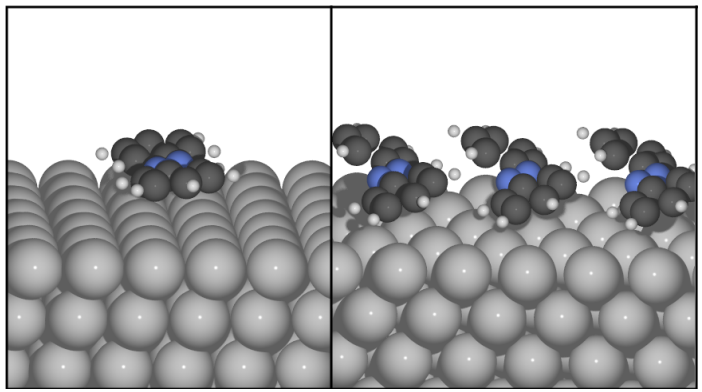
Comparison to X-Ray Standing Wave experiments

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

Adsorbate Structure







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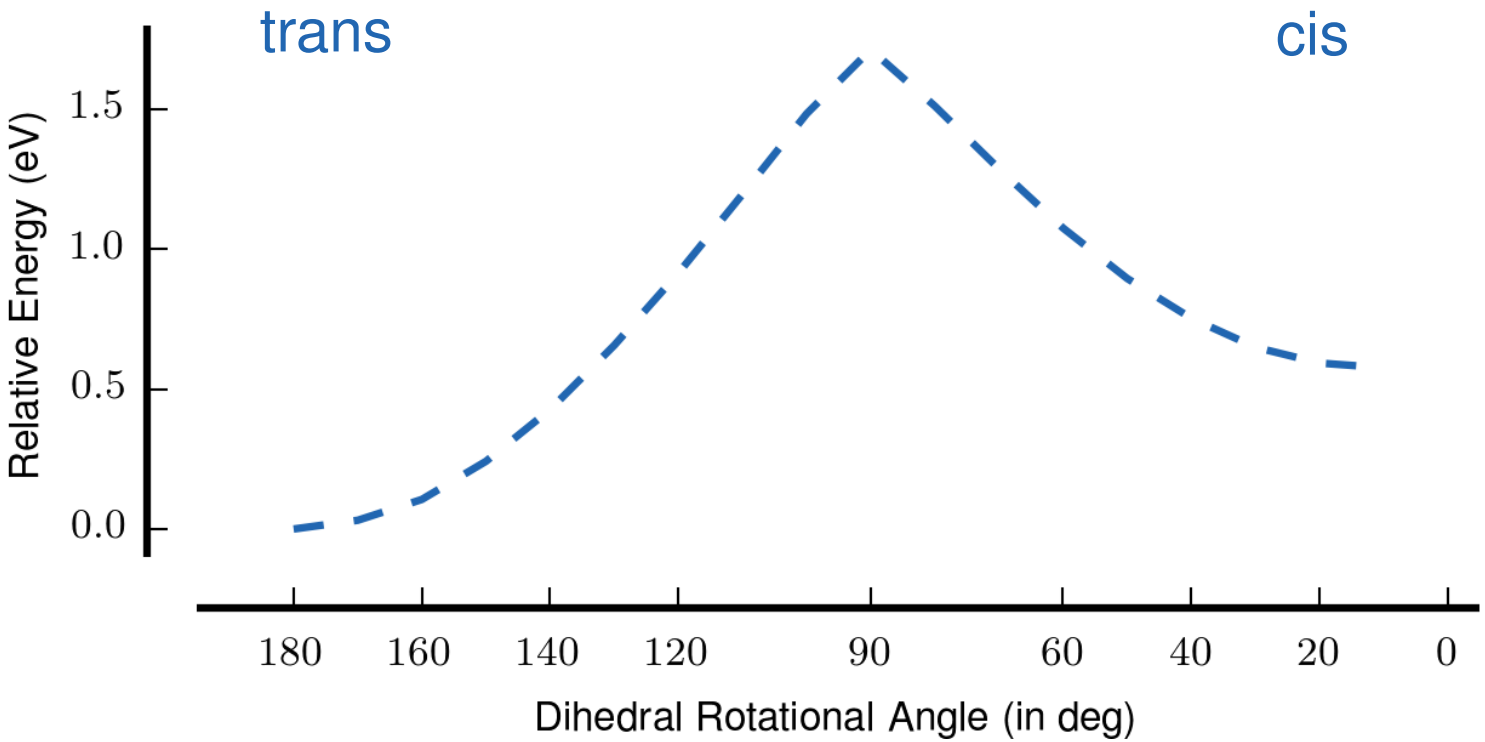
high cov. ($T = 210\ K$)	2.98	9.0	17.7
exp. ($T = 210\ K$)	2.97 ±0.05	−0.7 ±2.3	17.7 ±2.7

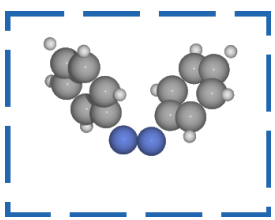
- exp. conditions = high coverage
- accurate adsorbate structure
- incl. anharmonic effects at finite T

Collaboration with Prof. Stefan Tautz, FZ Jülich
Comparison to X-Ray Standing Wave experiments

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

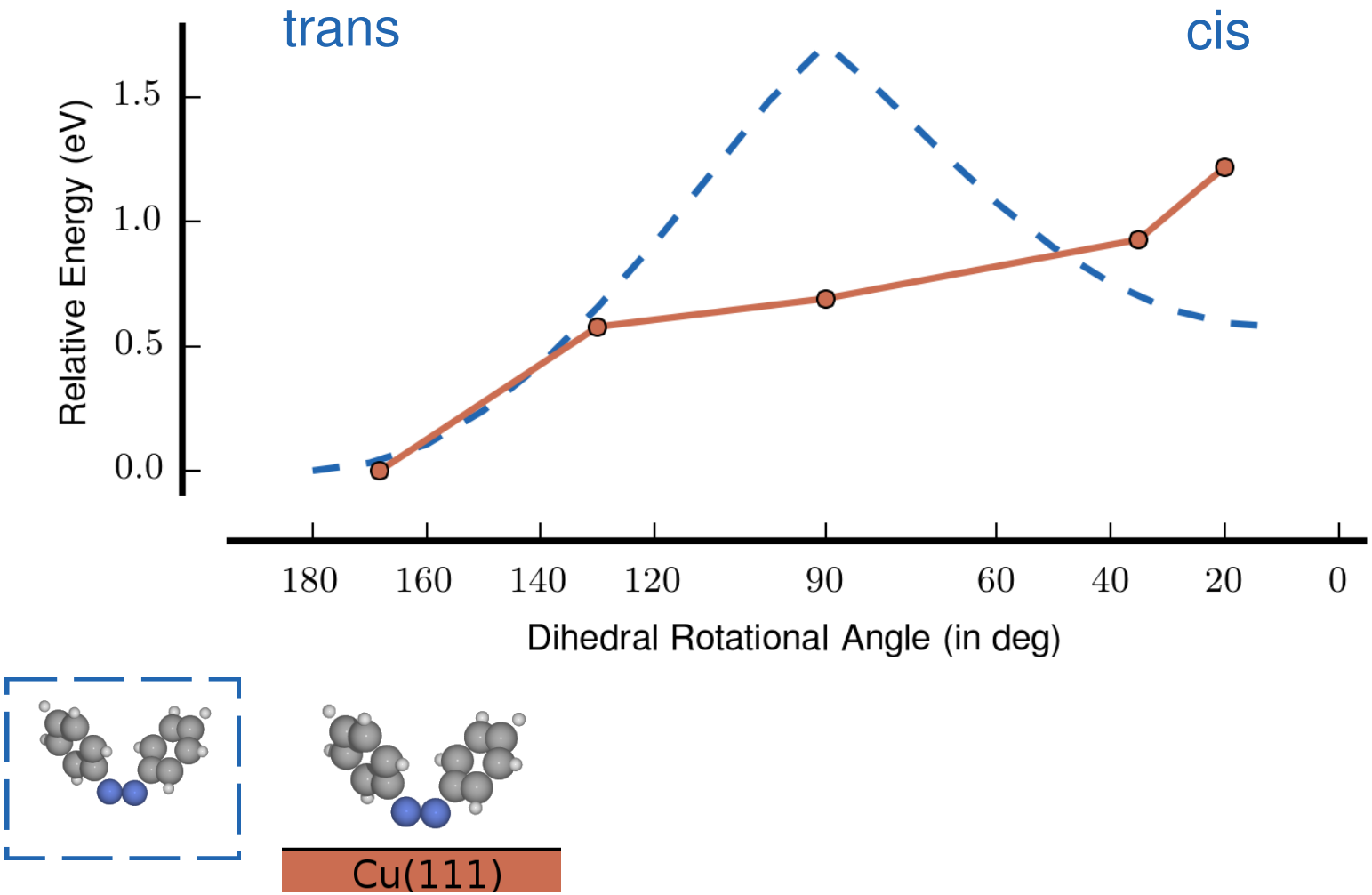
Molecule Bistability





Maurer, Reuter, Angew. Chem. Int. Ed. **51** (2012), 12009-12011.

Molecule Bistability



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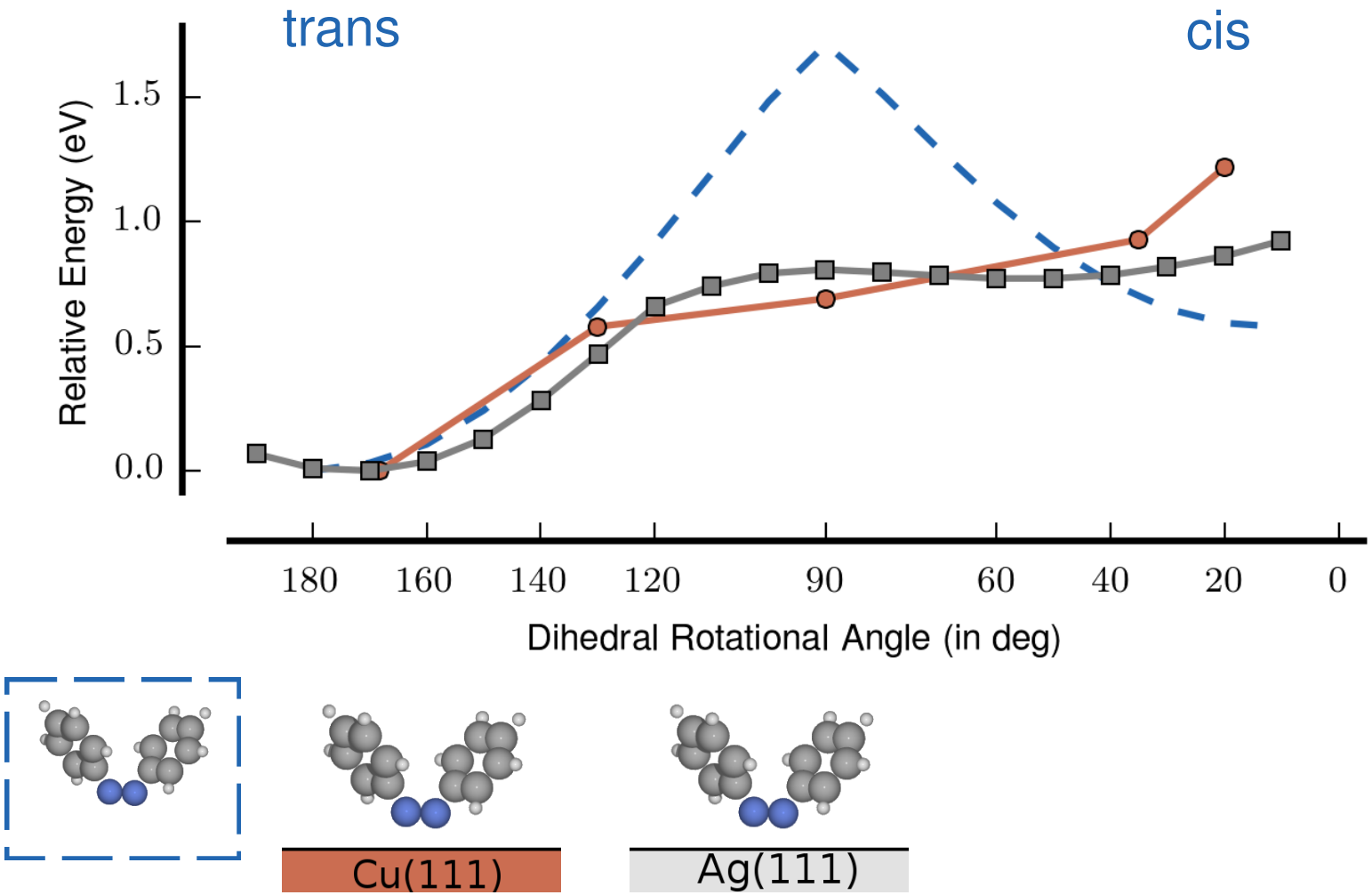

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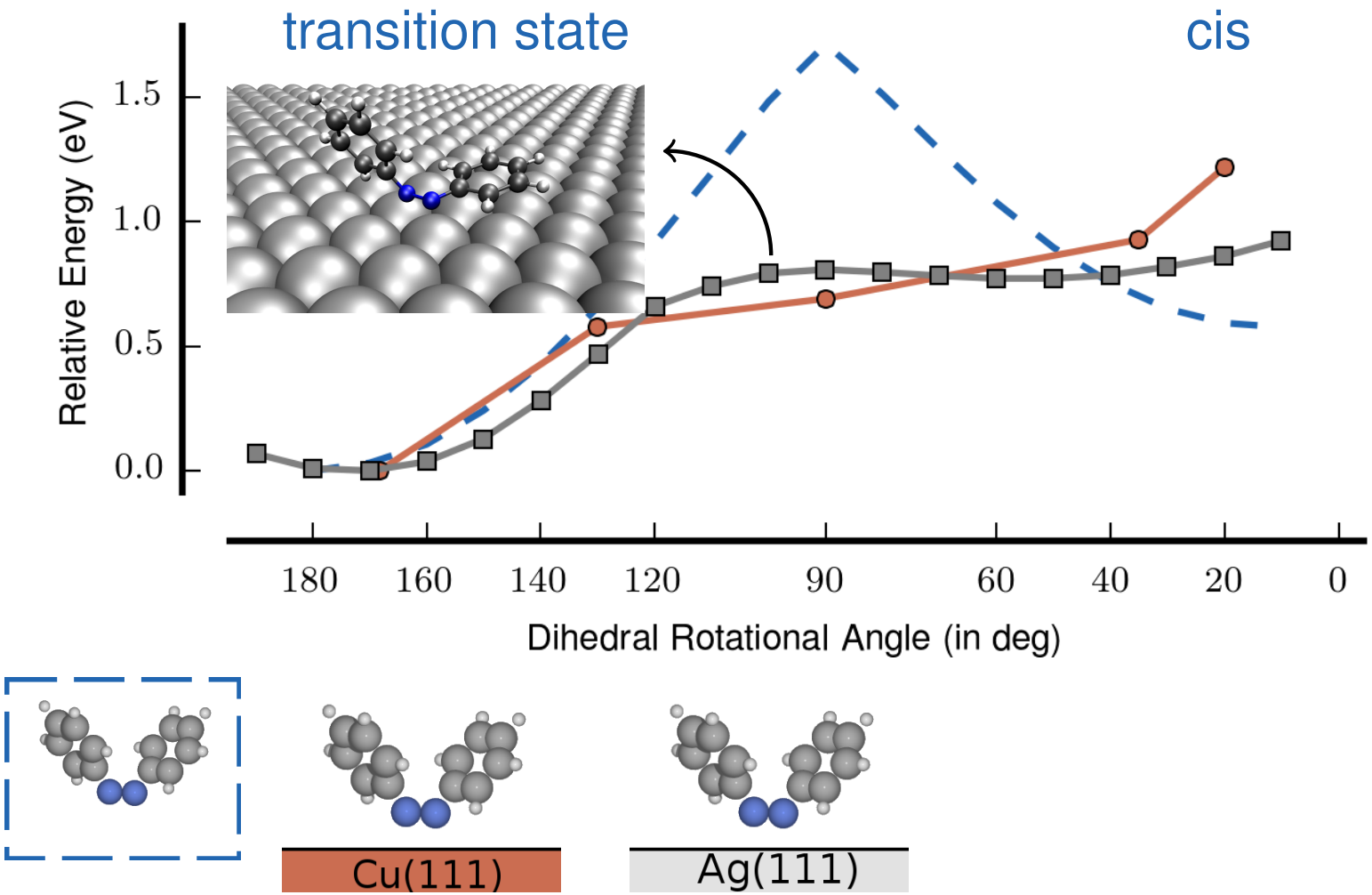

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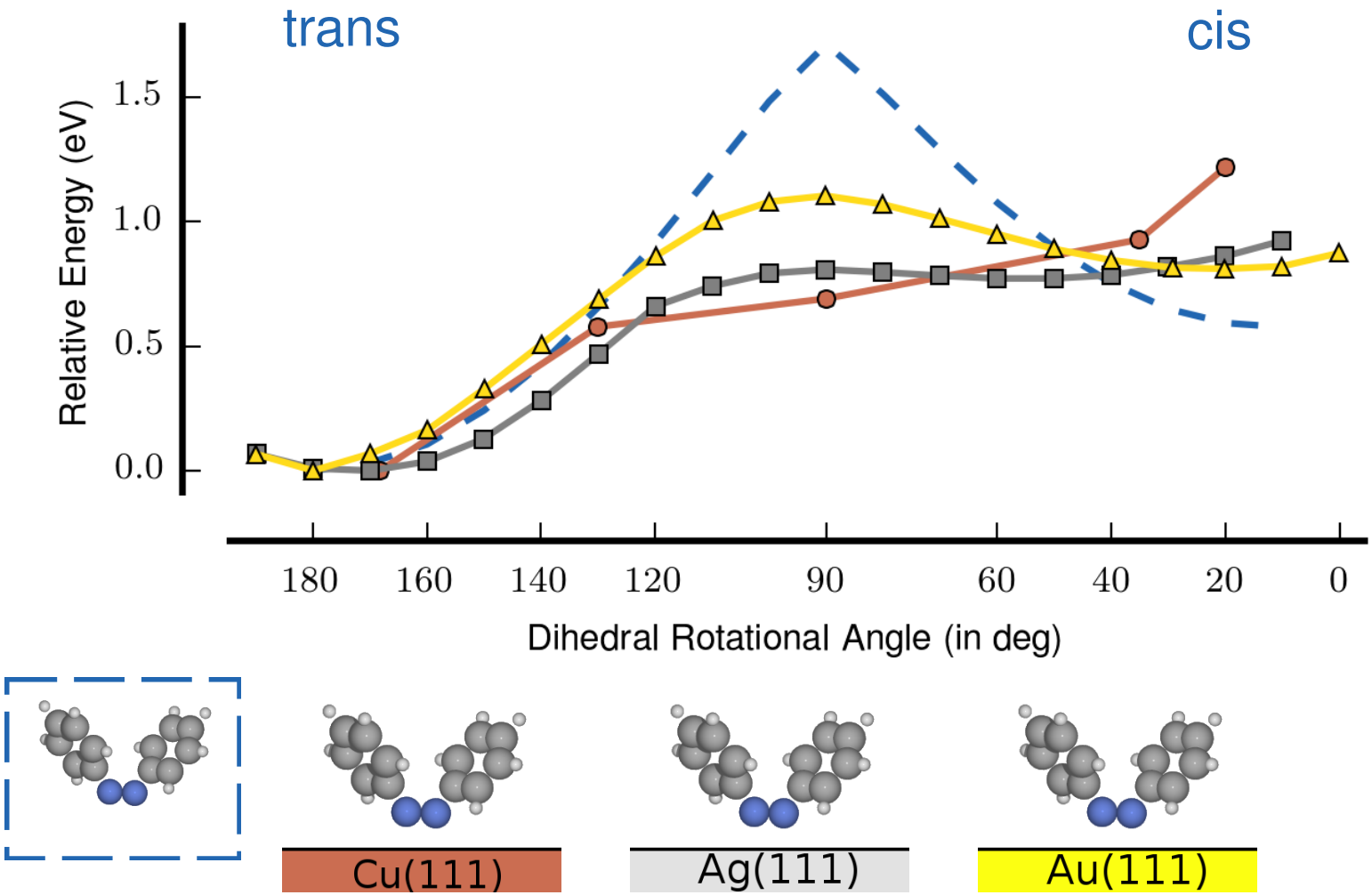

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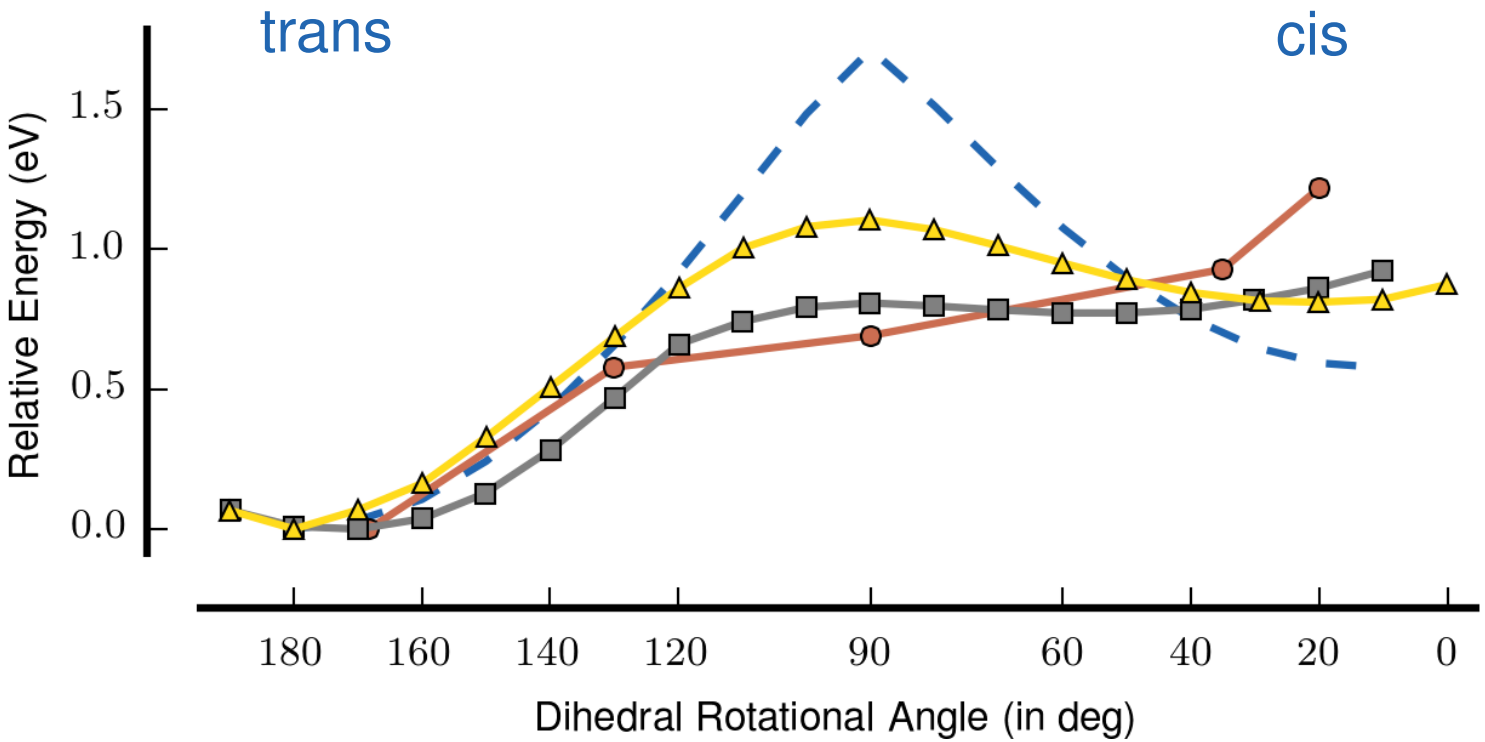
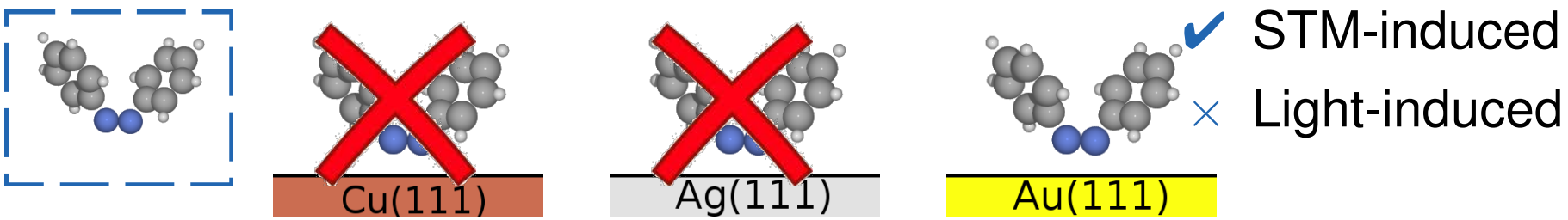
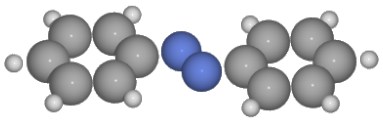


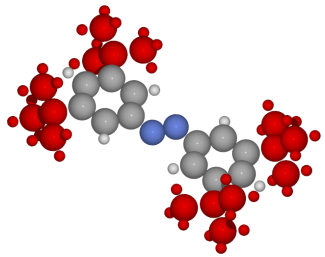


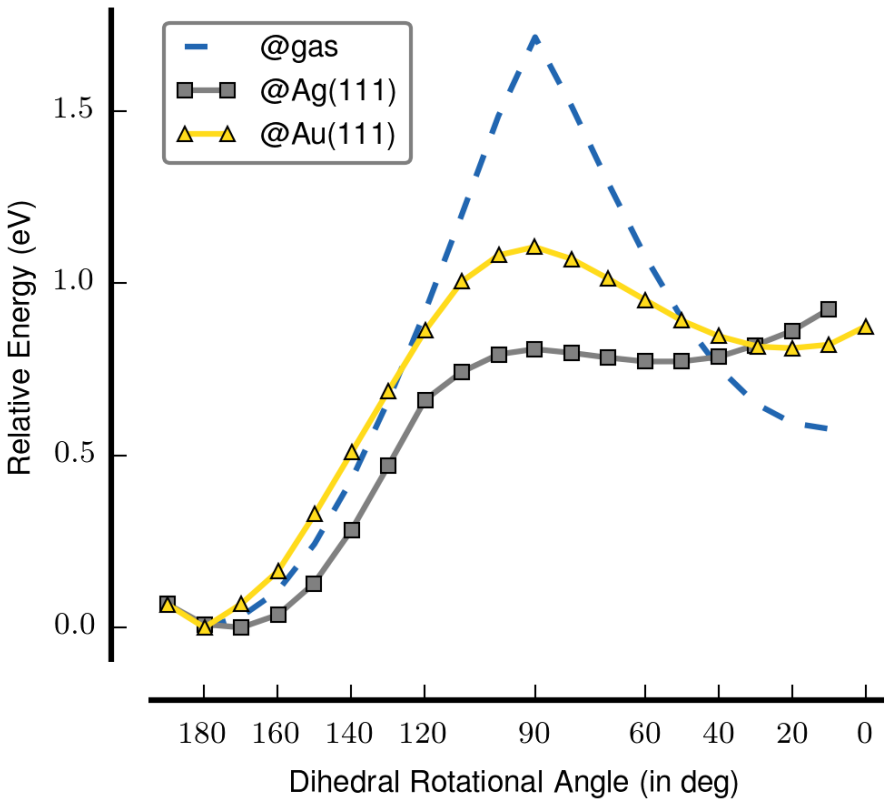
Groundstate Bistability is lost → cis-Ab not stable

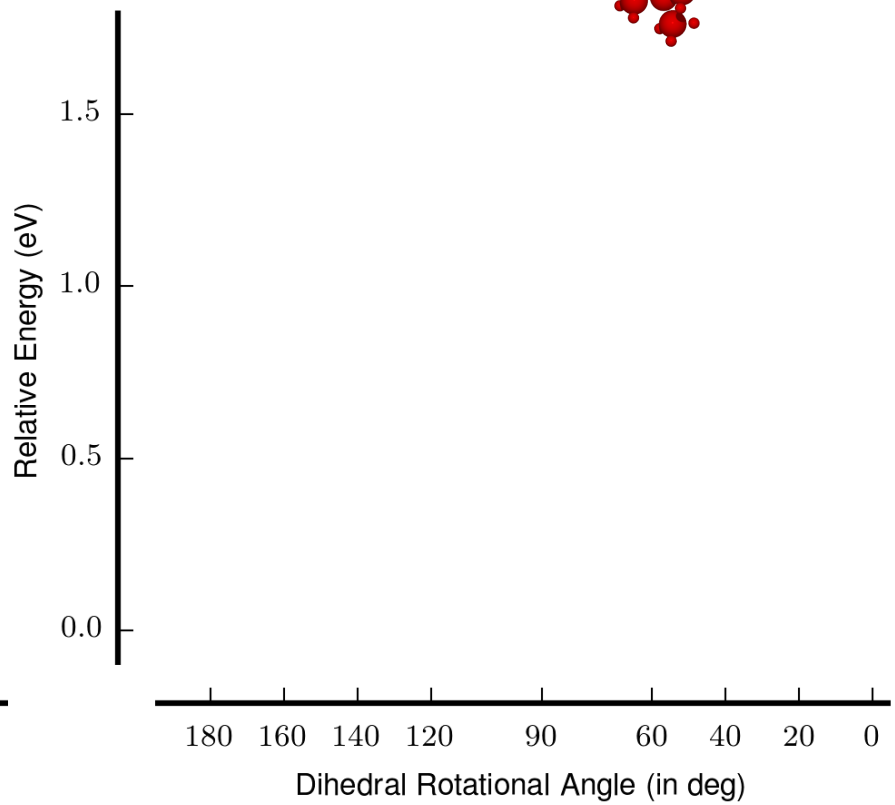
Maurer, Reuter, Angew. Chem. Int. Ed. **51** (2012), 12009-12011.

Molecule Functionalization



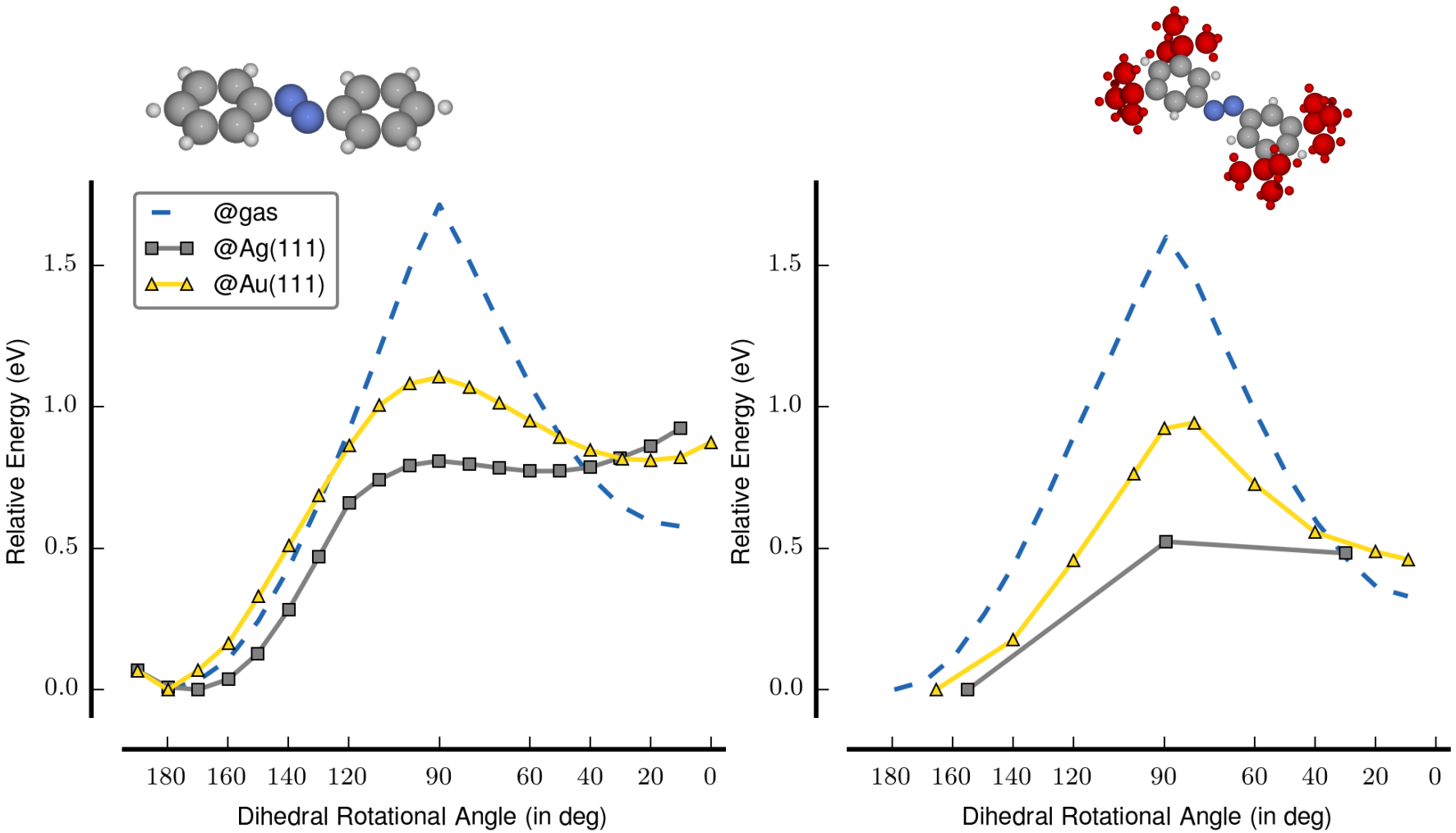






Maurer, Reuter, Angew. Chem. Int. Ed. **51** (2012), 12009-12011.

Molecule Functionalization

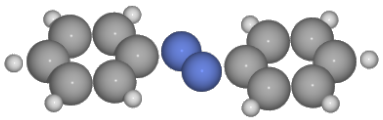


Maurer, Reuter, Angew. Chem. Int. Ed. **51** (2012), 12009-12011.

Molecule Functionalization

✔ STM

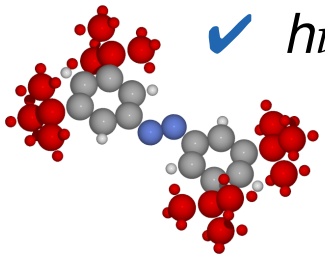
× $h\nu$

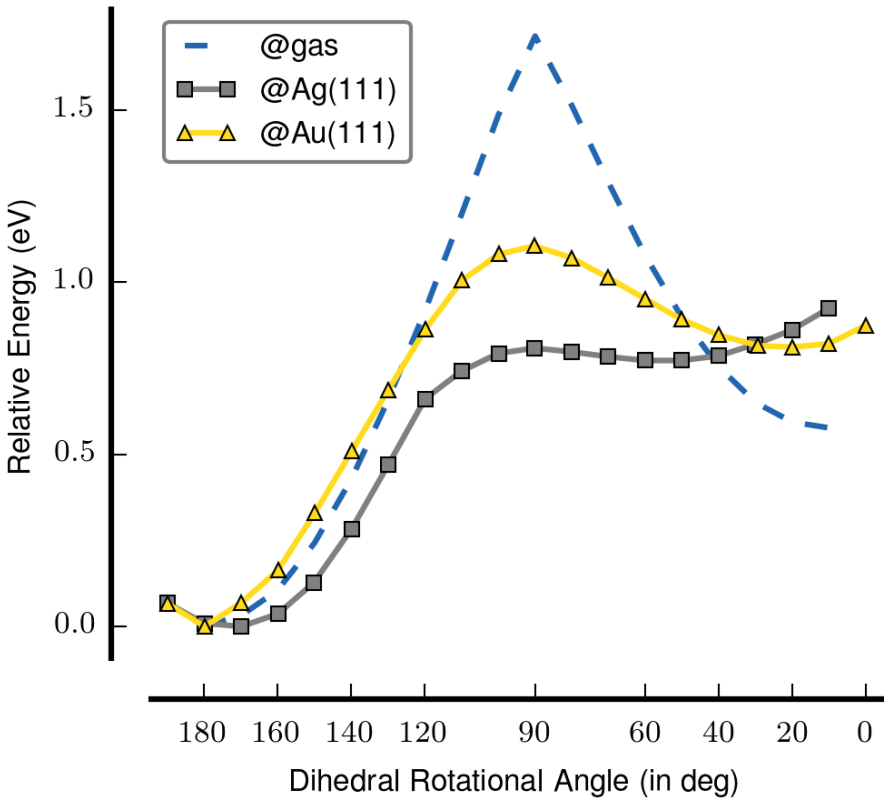


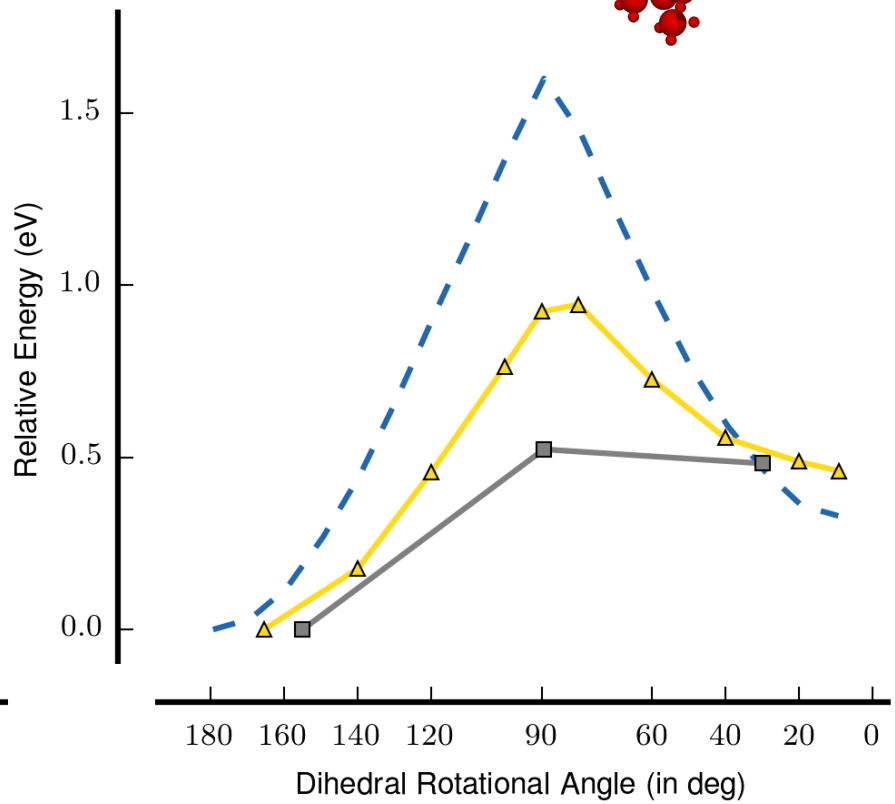
Spacer groups
→ no effect on stability
?excited state mechanism?

✔ STM

✔ $h\nu$







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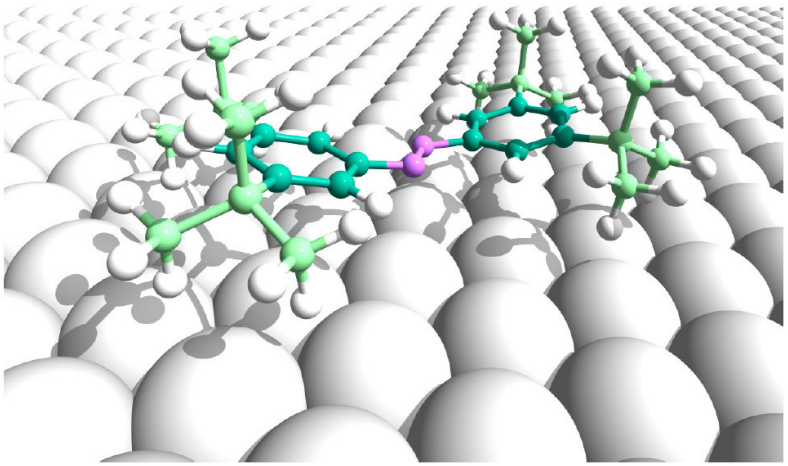
Efficient Excited State Methodology - ΔSCF ?



Accuracy

MBPT
TDDFT
ΔSCF DFT

Speed

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

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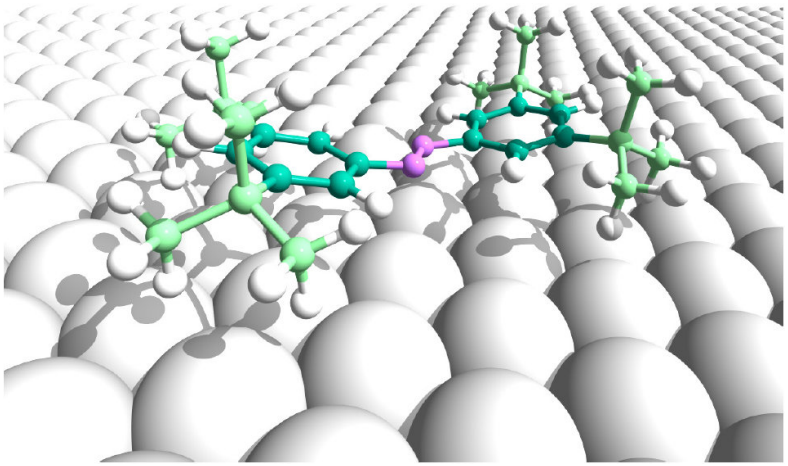

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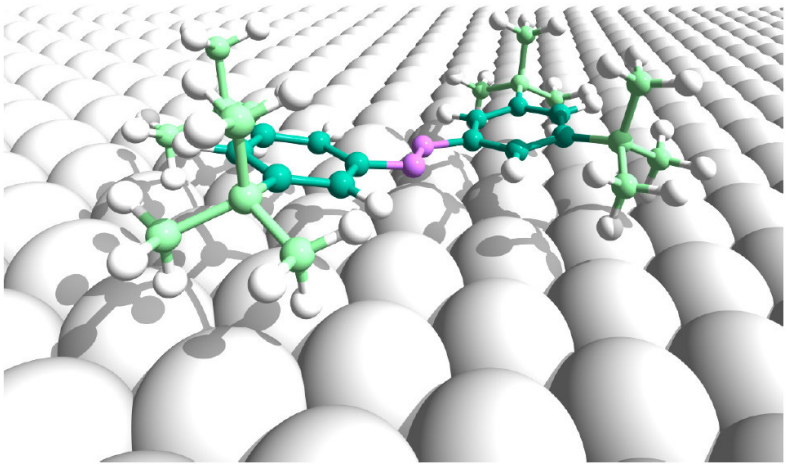

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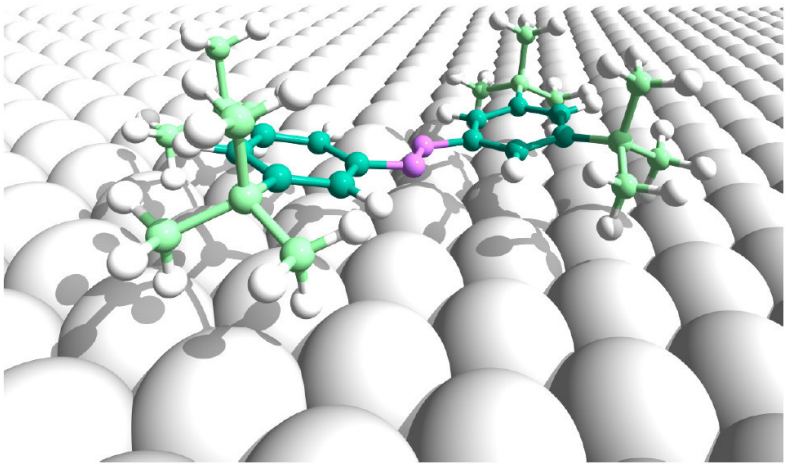

Constraining occupation of molecular states

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~~TDDFT~~
ΔSCF DFT

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

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

Gunnarsson, Lundqvist, PRB **13** (1976), 4274–4298.
Jones, Gunnarsson, Rev. Mod. Phys. **61** (1989), 689–746.

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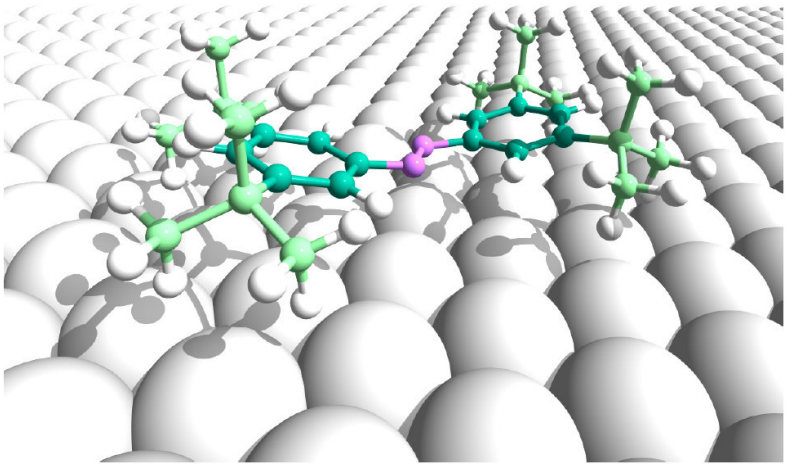

Constraining occupation of molecular states

- Molecular states on the surface?

Accuracy ↑ Speed ↓

~~MBPT~~
~~TDDFT~~
ΔSCF DFT

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

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

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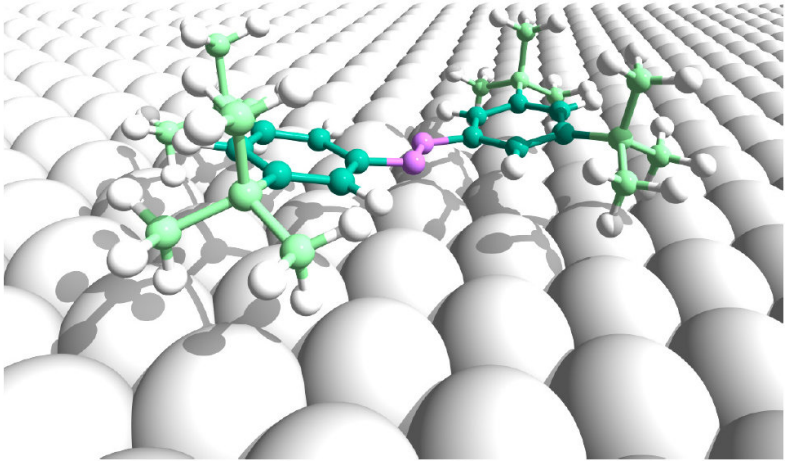

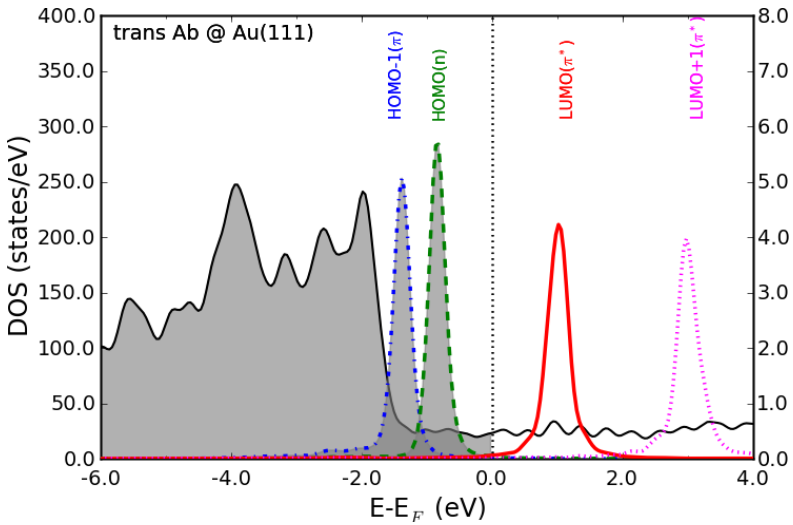

McNellis *et al.*, PCCP **111** (2010), 6404-6412.
McNellis *et al.*, PRB **80** (2009), 035414.

Accuracy ↑ Speed ↓

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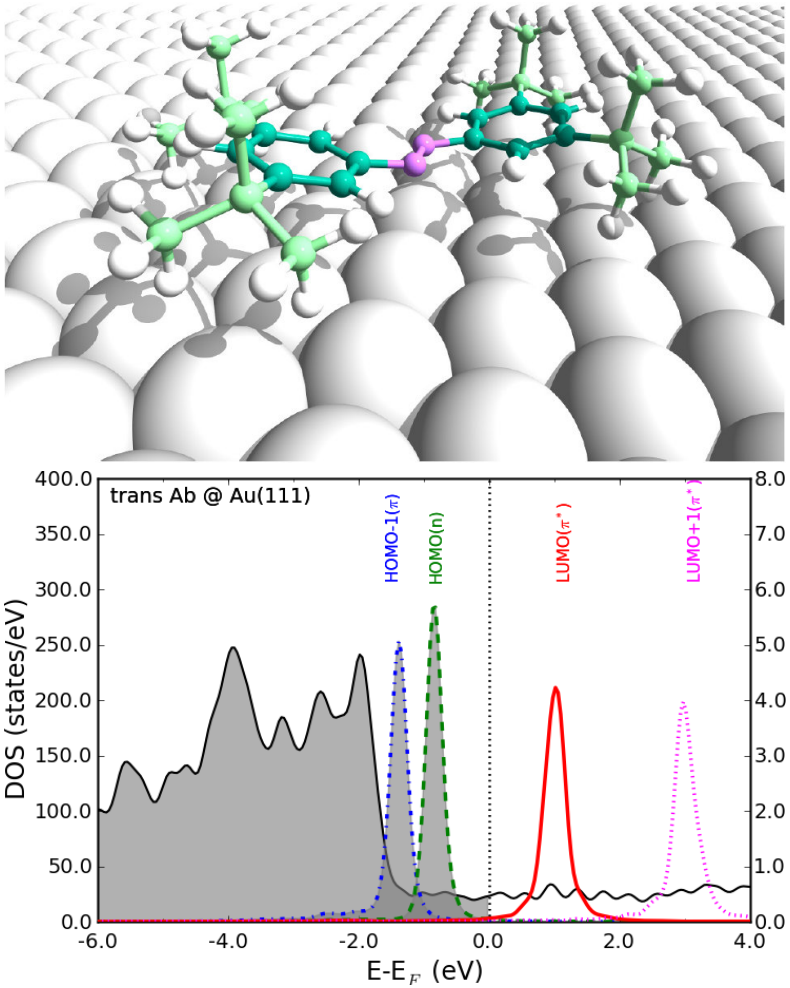
Efficient Excited State Methodology - leΔSCF !



Accuracy

~~MBPT~~

~~TDDFT~~

leΔSCF DFT

Speed

$$|\psi_c> = \sum_i |\psi_i><\psi_i|\phi_c>$$

$$\rho = \sum_i f_i |\psi_i'><\psi_i'| + f_c|\psi_c><\psi_c|$$

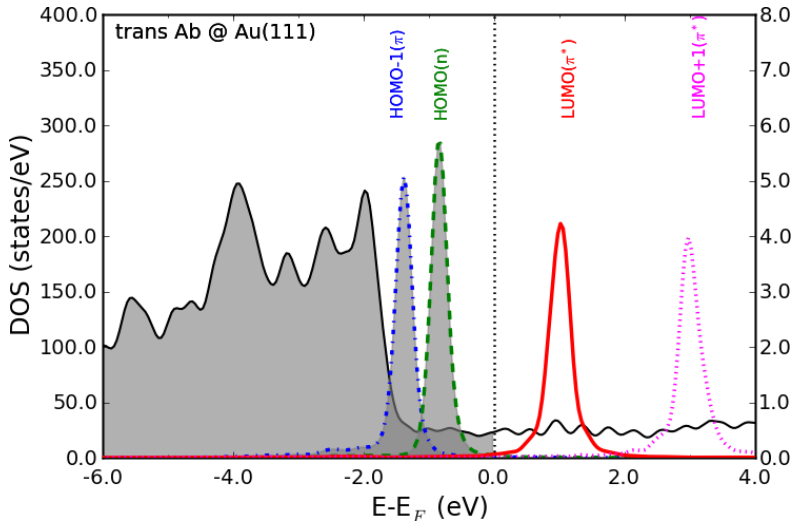
ϕ_c ... Gasphase molecular orbital

$$\sum_i f_i + \sum_c f_c = N_e$$

Gavnholt *et al.*, PRB **78** (2008), 075441.

Maurer and Reuter, JCP **139** (2013), 014708.

Excited State Method - leΔSCF



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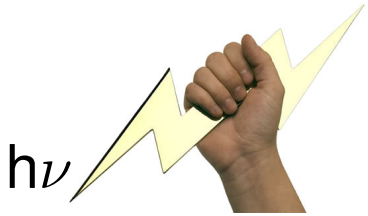
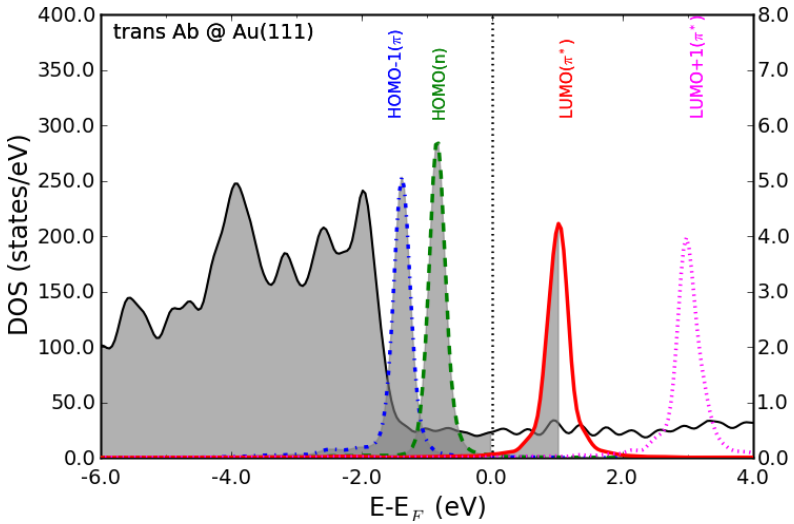


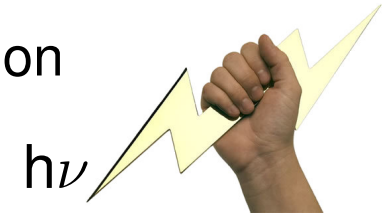


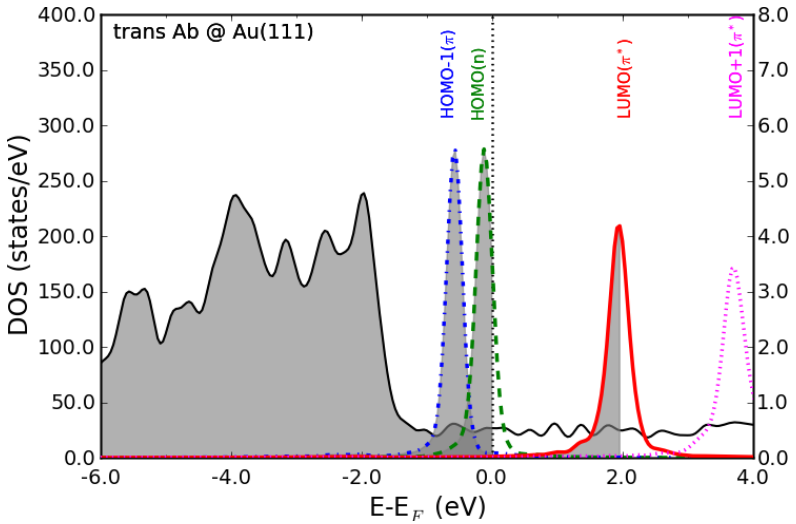
Maurer and Reuter, JCP **139** (2013), 014708.

Excited State Method - leΔSCF

leΔSCF

Orbital relaxation





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Excited State Method - leΔSCF

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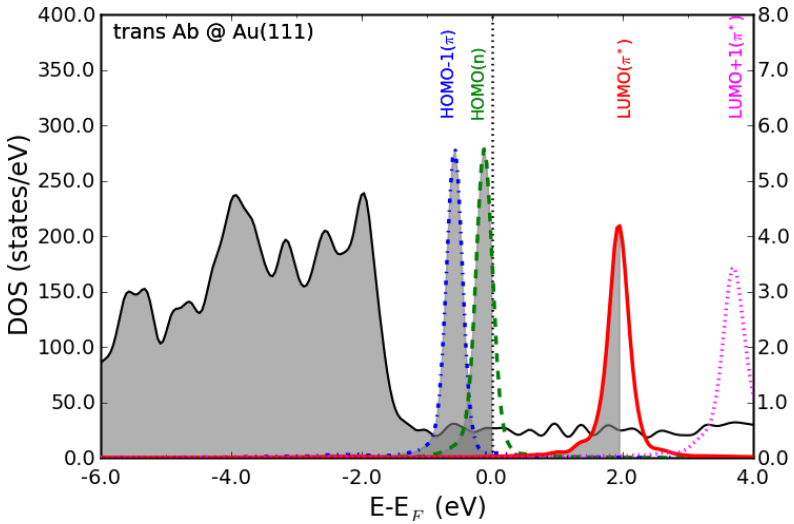

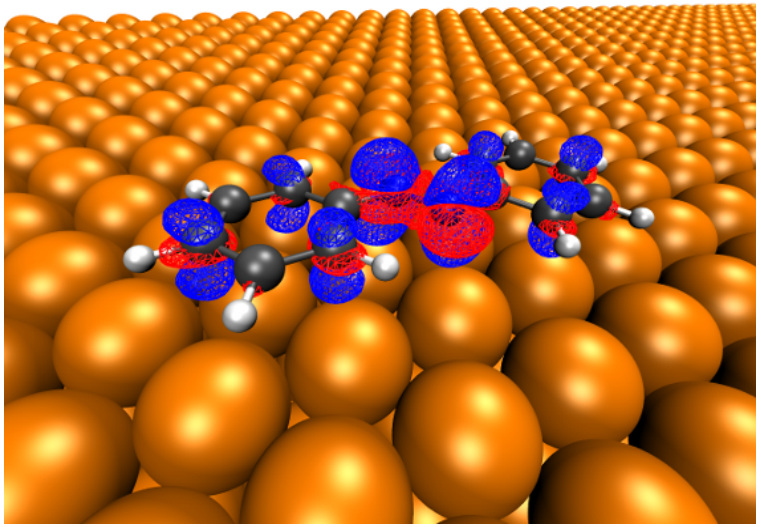

$\Rightarrow \quad E_{ex}$

Maurer and Reuter, JCP **139** (2013), 014708.

Excited State Method - leΔSCF

leΔSCF

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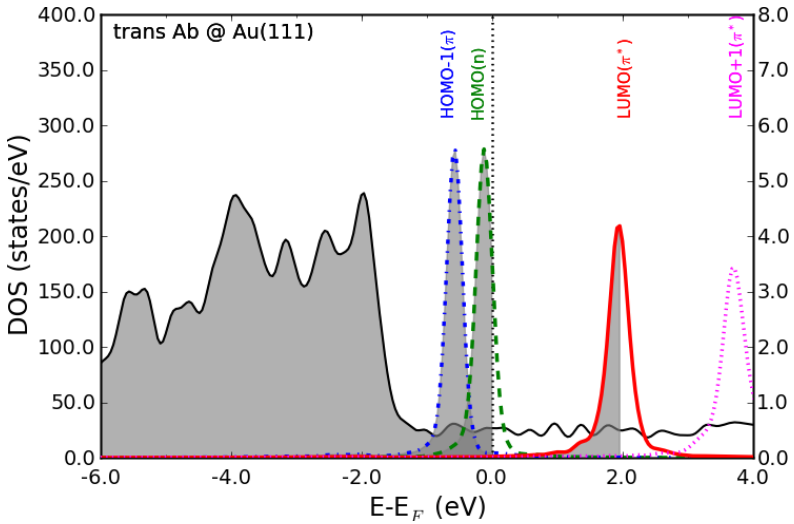
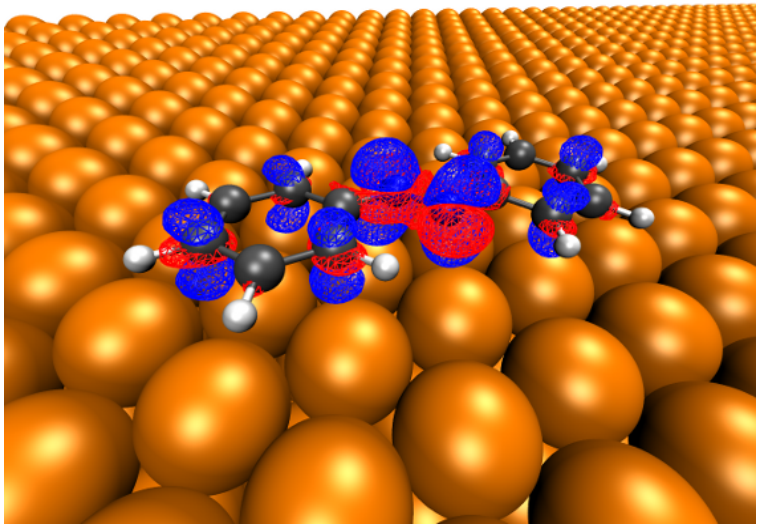




$\Rightarrow \quad E_{ex}$

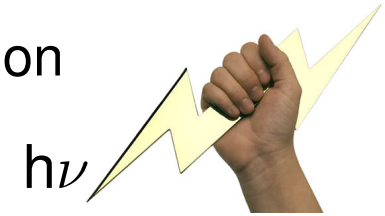
allows to treat
neutral excitations (n/$\pi \rightarrow \pi^*$)
'charged' excitations (metal$\rightarrow \pi^*$)

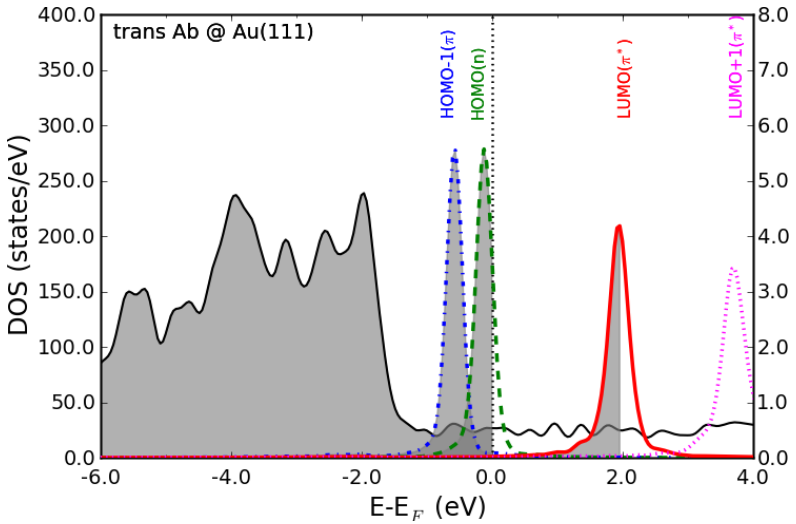
Maurer and Reuter, JCP **139** (2013), 014708.

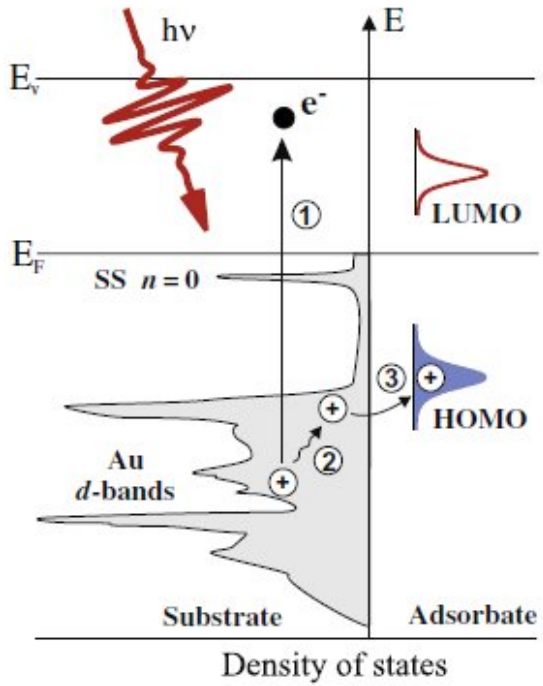
Excited State Method - leΔSCF

leΔSCF

Orbital relaxation







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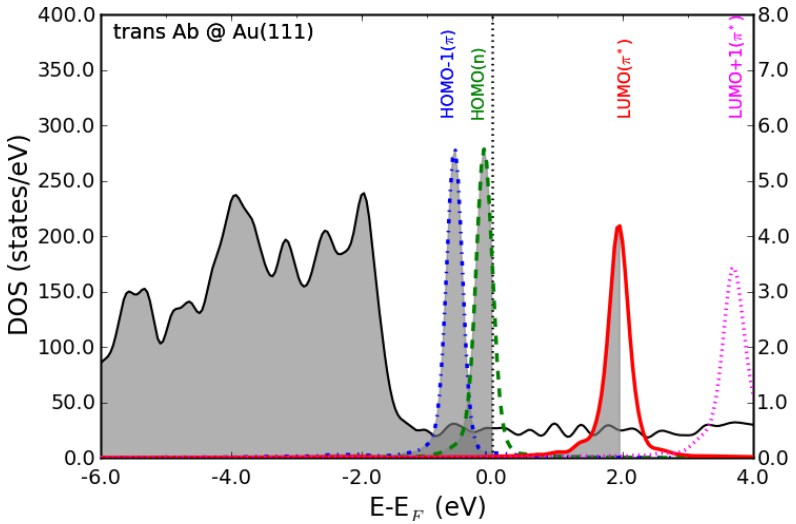
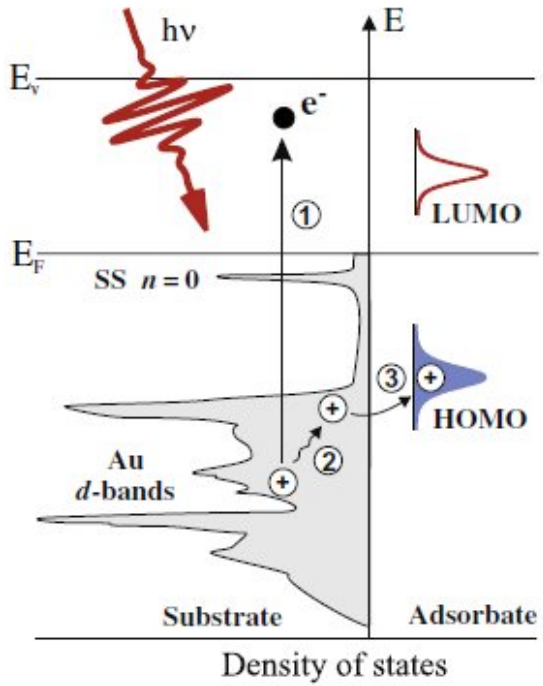
Maurer and Reuter, JCP **139** (2013), 014708.

Excited State Method - leΔSCF

correctly describes state shifts and image charge effects





separated systems:
!leΔSCF = ΔSCF!

allows to treat
neutral excitations (n/$\pi \rightarrow \pi^*$)
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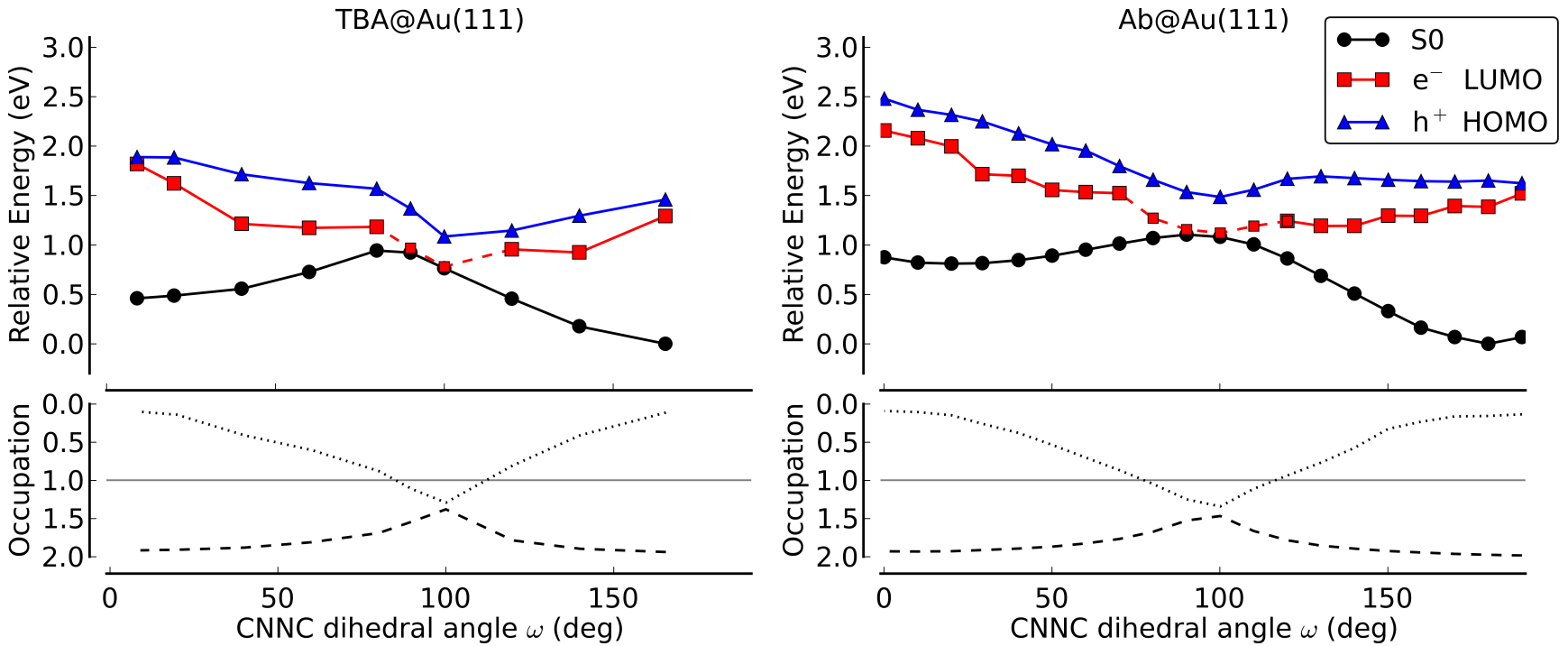
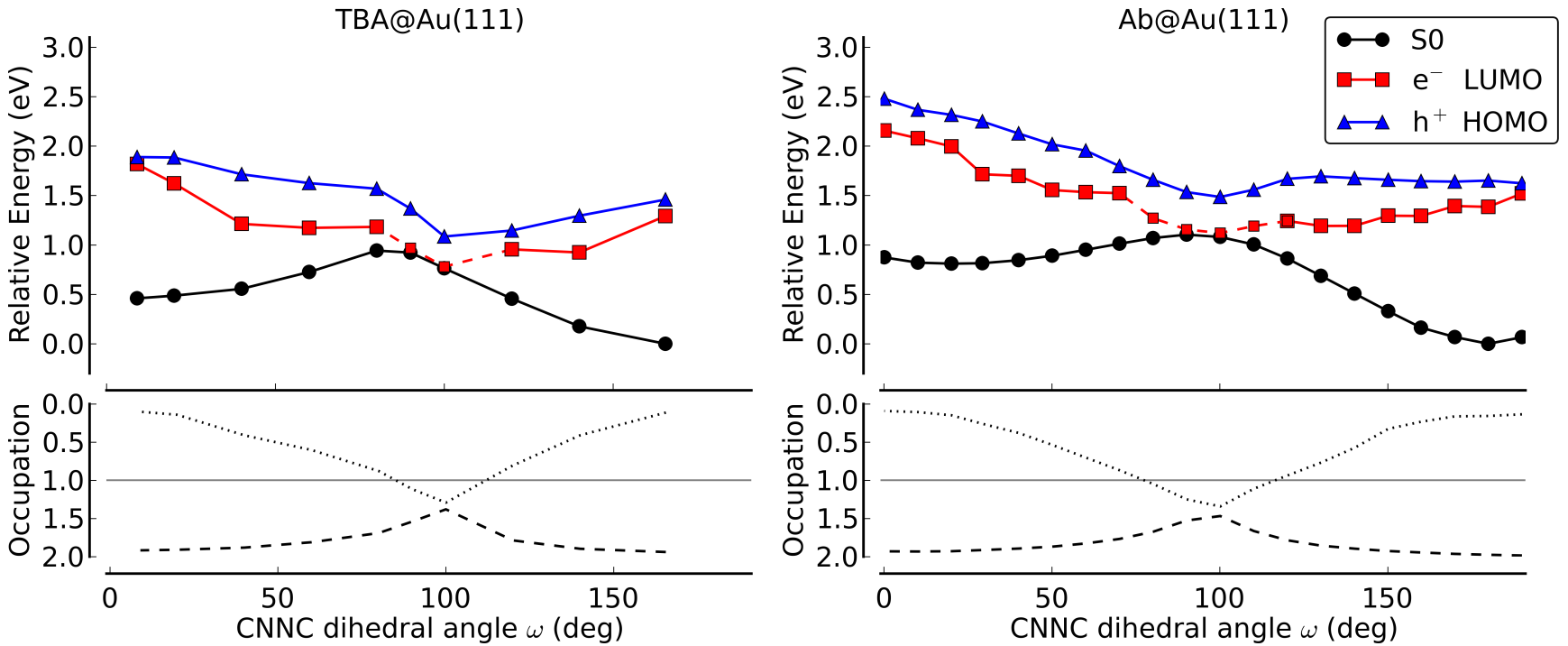
Maurer and Reuter, JCP **139** (2013), 014708.

Excited State Energetics - First Hints



? Shallow PESs $\rightarrow$ Enough E_{kin} collected in $\sim$40 fs ?

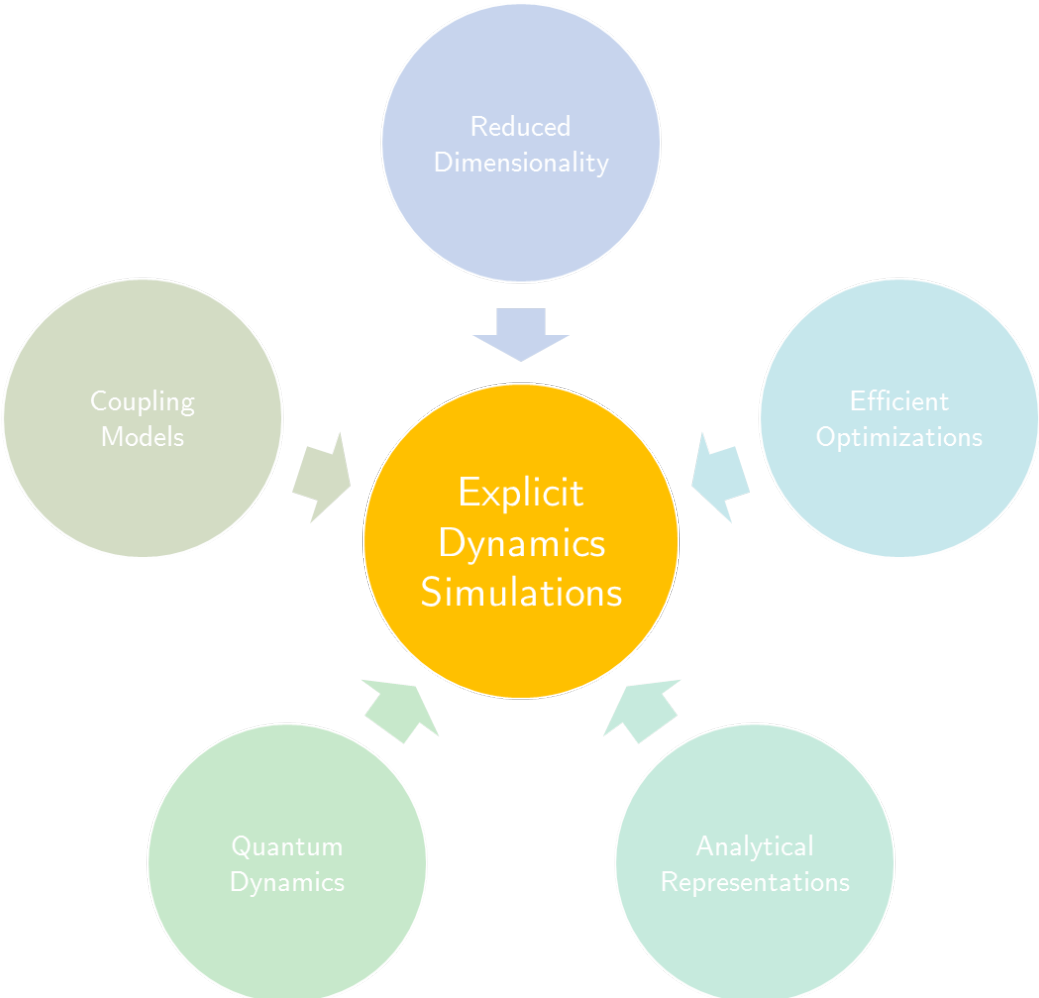
Excited State Energetics - First Hints



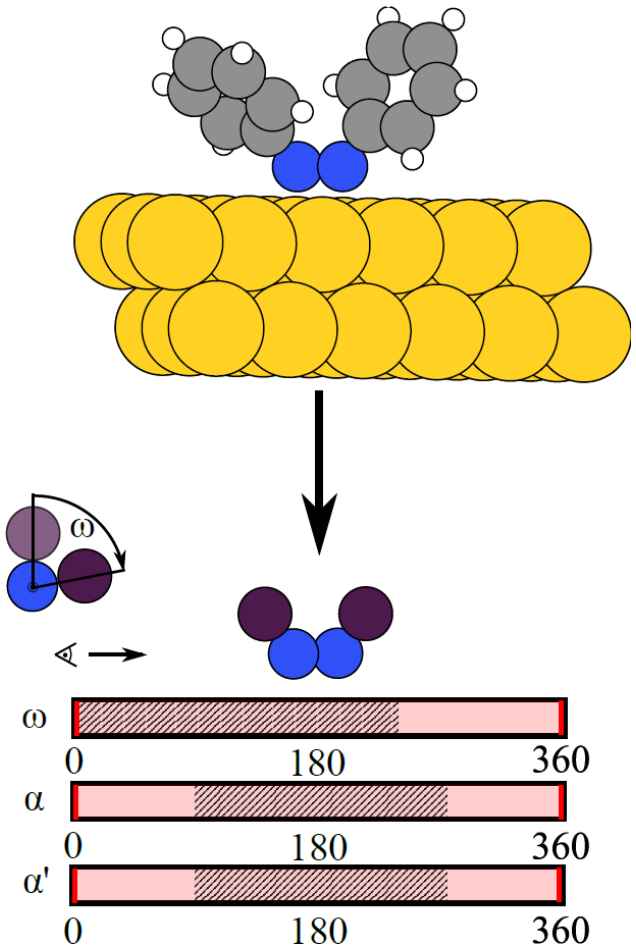
? Shallow PESs $\rightarrow$ Enough E_{kin} collected in $\sim$40 fs ?

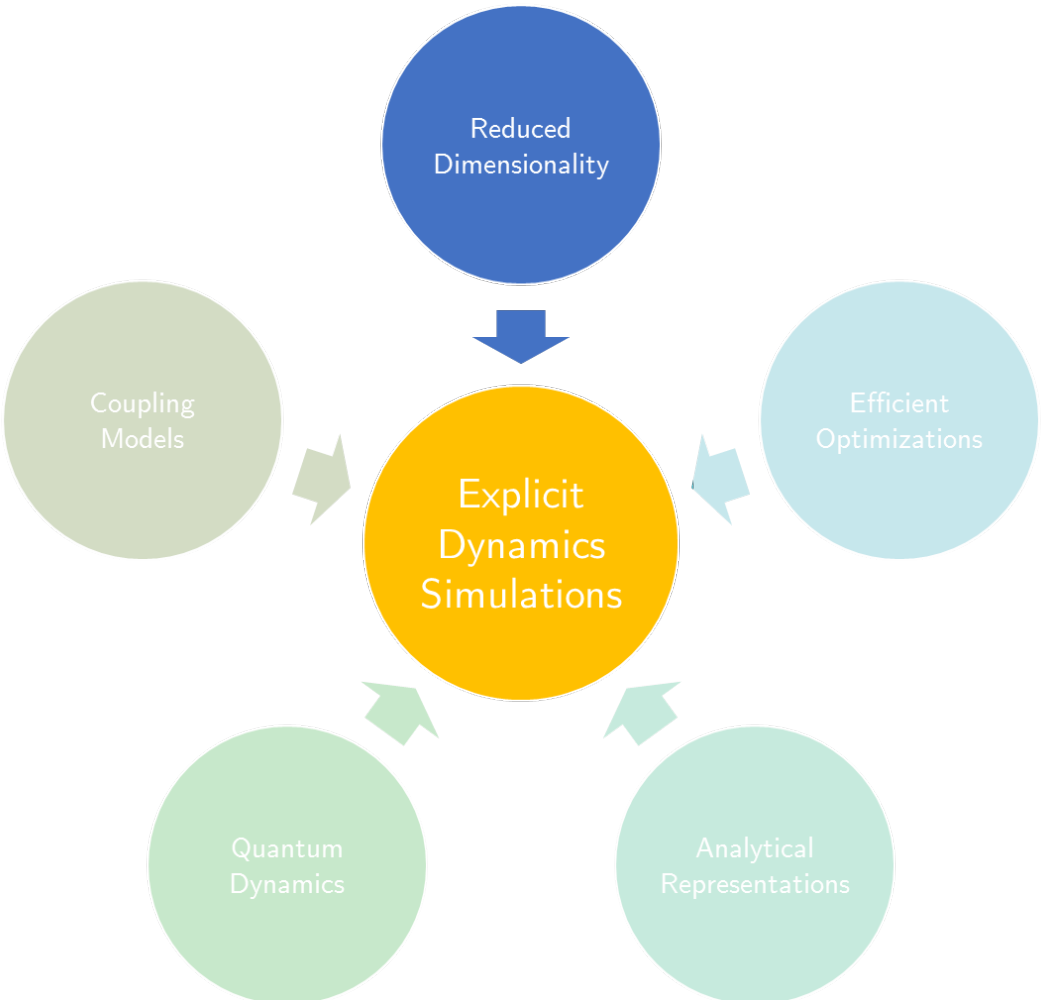
! $\rightarrow$ Dynamics simulations required !

Explicit Dynamics Simulations



Reduced Dimensionality





Explicit Dynamics Simulations

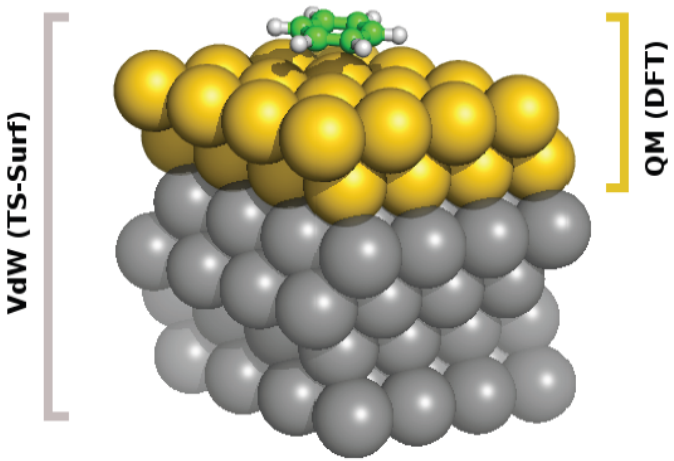
Efficient Optimizations

- Preoptimizations:

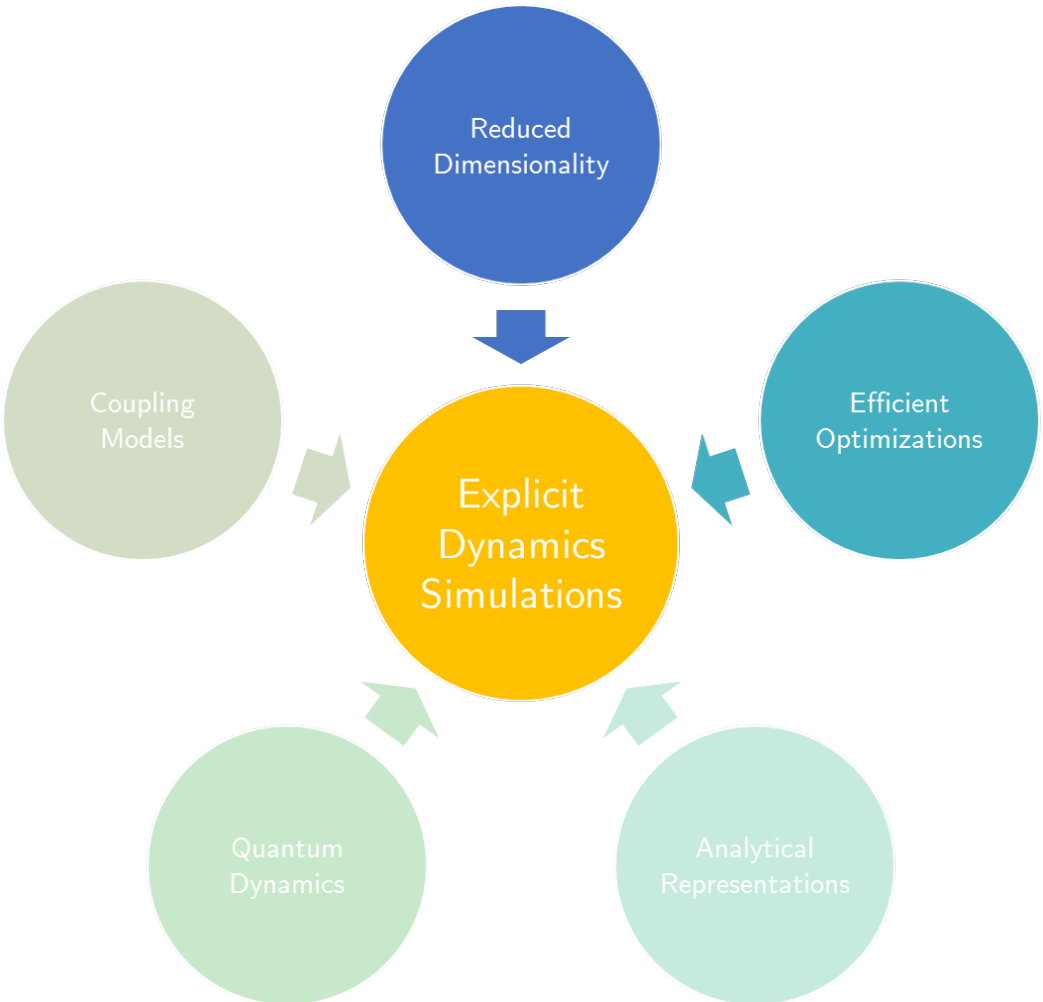
Force-Fields, Tight-Binding

- Increasing Efficiency:

vdW Embedding



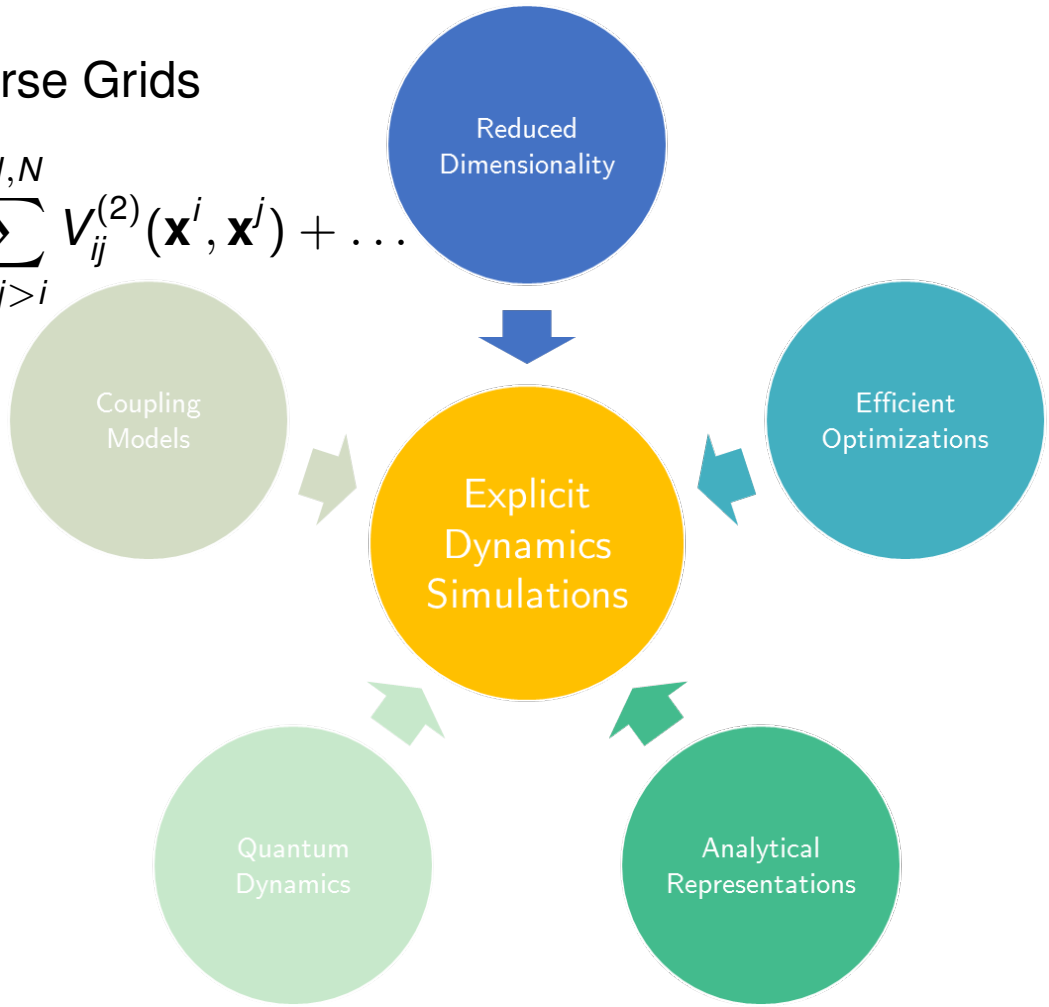
Masters Thesis: Georg Michelitsch



Analytical Representations

- Many-Body-Expansion / Sparse Grids

$$V(\mathbf{x}) = V^{(0)} + \sum_{i}^{N} V_i^{(1)}(\mathbf{x}) + \sum_{i,j>i}^{N,N} V_{ij}^{(2)}(\mathbf{x}^i, \mathbf{x}^j) + \dots$$



Strobusch, Scheurer, JCP, *140*, 074111 (2014)

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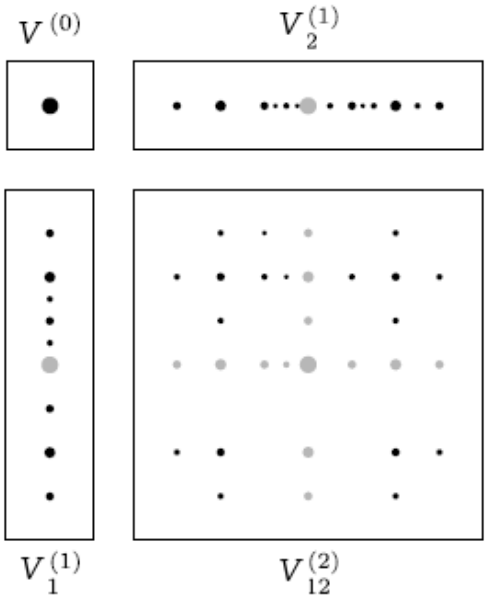

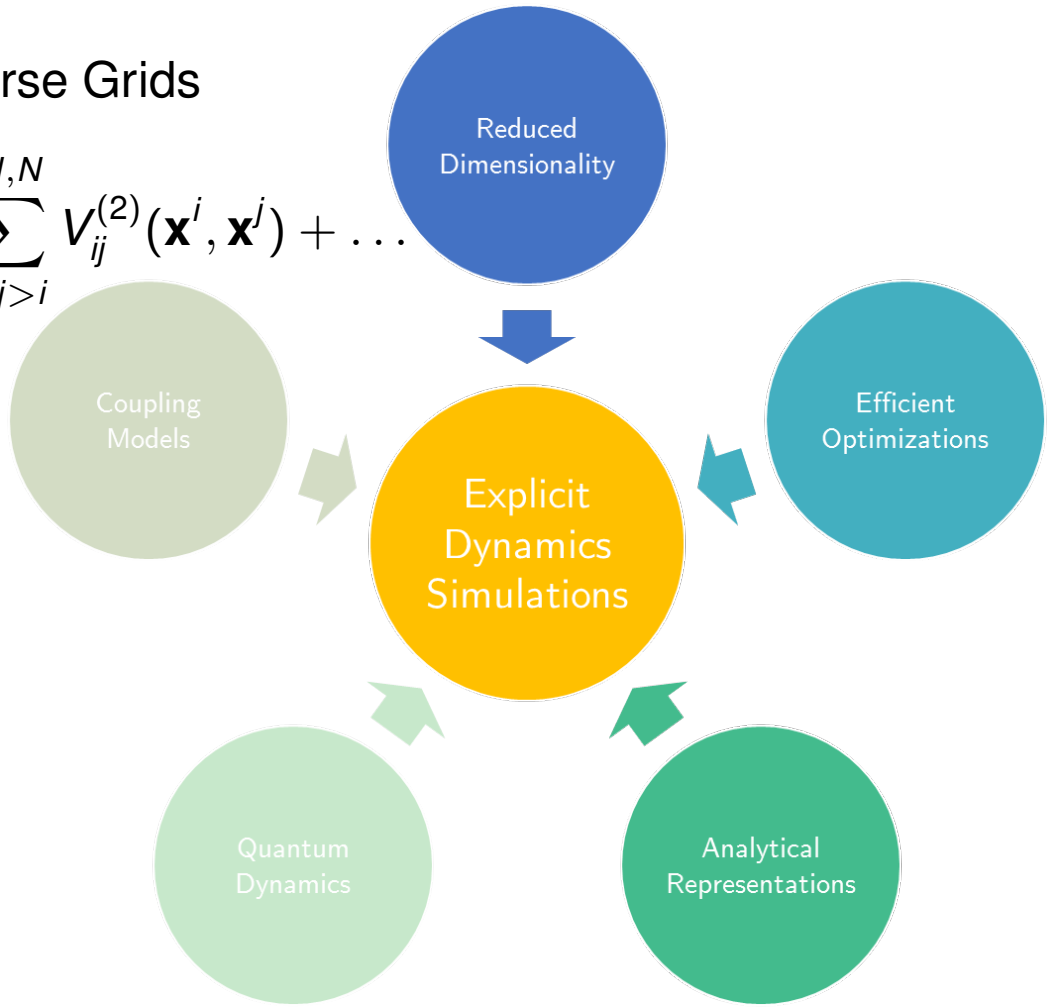

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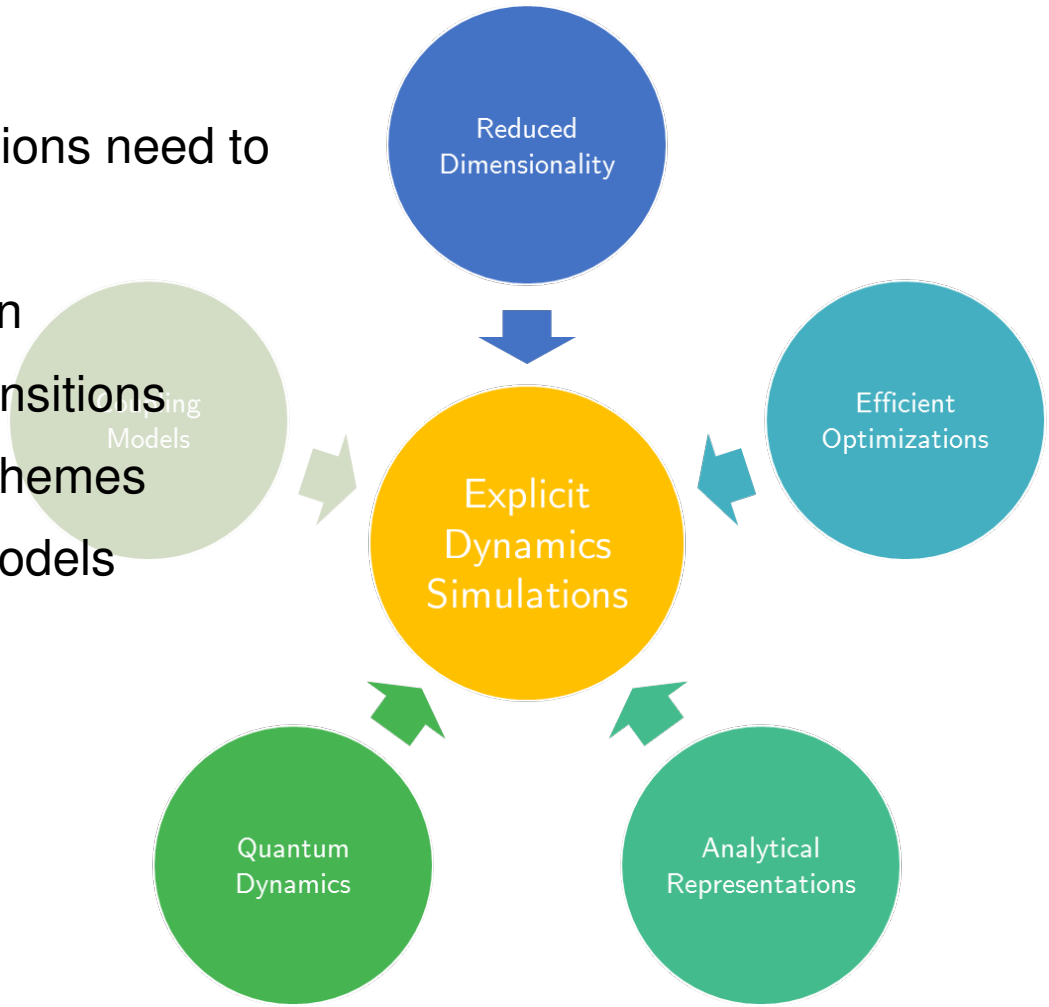
Quantum Dynamics

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



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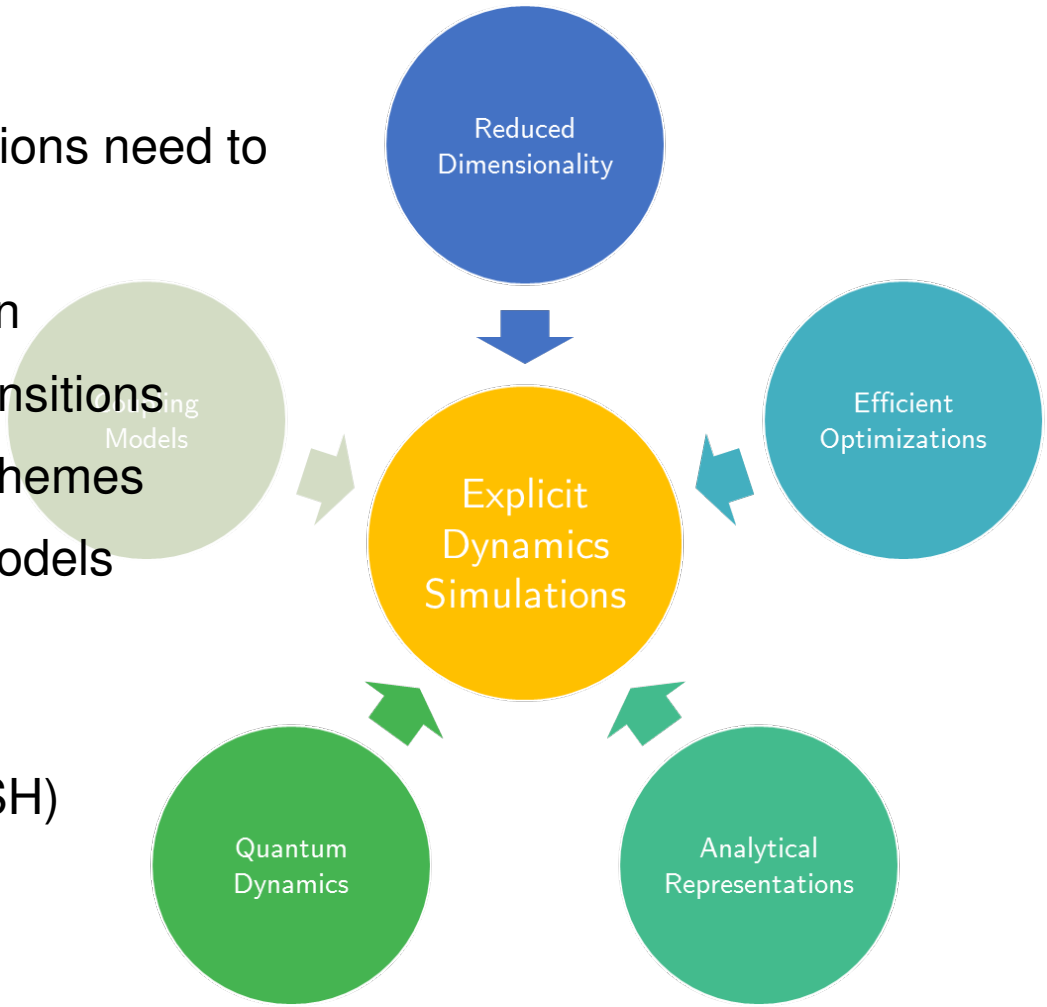
⇒ Trajectory-Surface Hopping (TSH)
⇒ Independent-Electron TSH



Tully, JCP, *93*, 1061 (1990); Shenvi, Roy, Tully, JCP, *130*, 174107 (2009)

Coupling Models

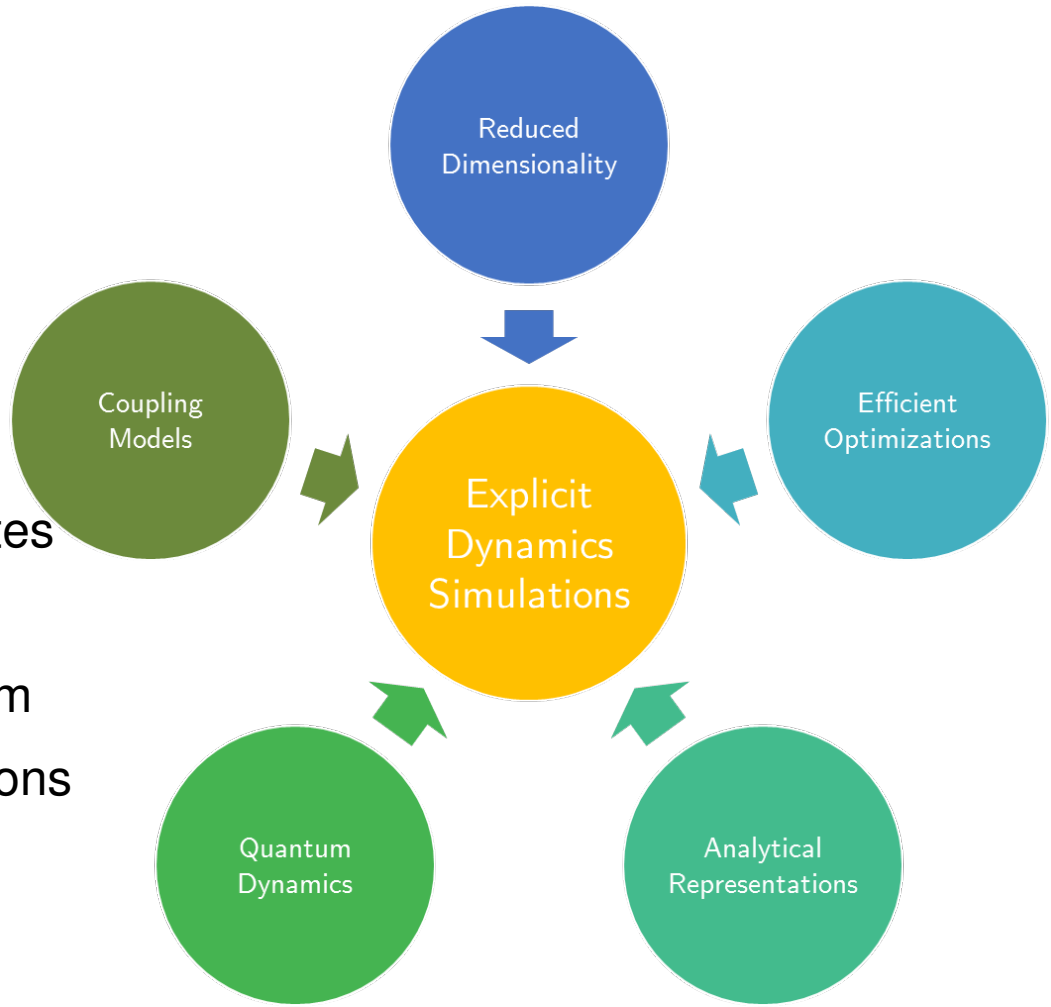
Need to account for

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.
Maurer, Reuter, Angew. Chem. Int. Ed. **51** (2012), 12009-12011.
Maurer and Reuter, JCP **139** (2013), 014708.
Gopakumar *et al.* Angew. Chem. Int. Ed. 52 (2013), 11007–11010.
Maurer and Reuter, JCP **135** (2011), 224303.

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- ...perform explicit dynamical simulation of photoswitching

Thank you for your attention!

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