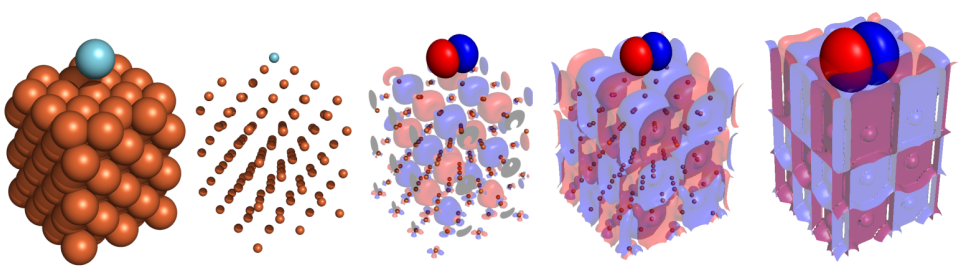
FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

Interpreting Ultrafast Electron Transfer on Surfaces with a Converged First-Principles Newns-Anderson Chemisorption Function

FHI-aims Users and Developers Meeting, Hamburg, August 2-4th, 2023.

Simiam Ghan, Elias Diesen, Christian Kunkel, Karsten Reuter and Harald Oberhofer



$$H_{ad} = \langle \psi_a | \hat{H} | \psi_d \rangle$$

Density Functional Theory

- The workhorse of computational physics & chemistry[1]
- **Delocalized electronic structure**
  - **Limited interpretability**

Interpretative Schemes

- Charge analysis: Mulliken, Bader, Hirshfeld
- Bond-order analysis: Mulliken [2], COOP, COHP
- PDOS, LDOS, MODOS

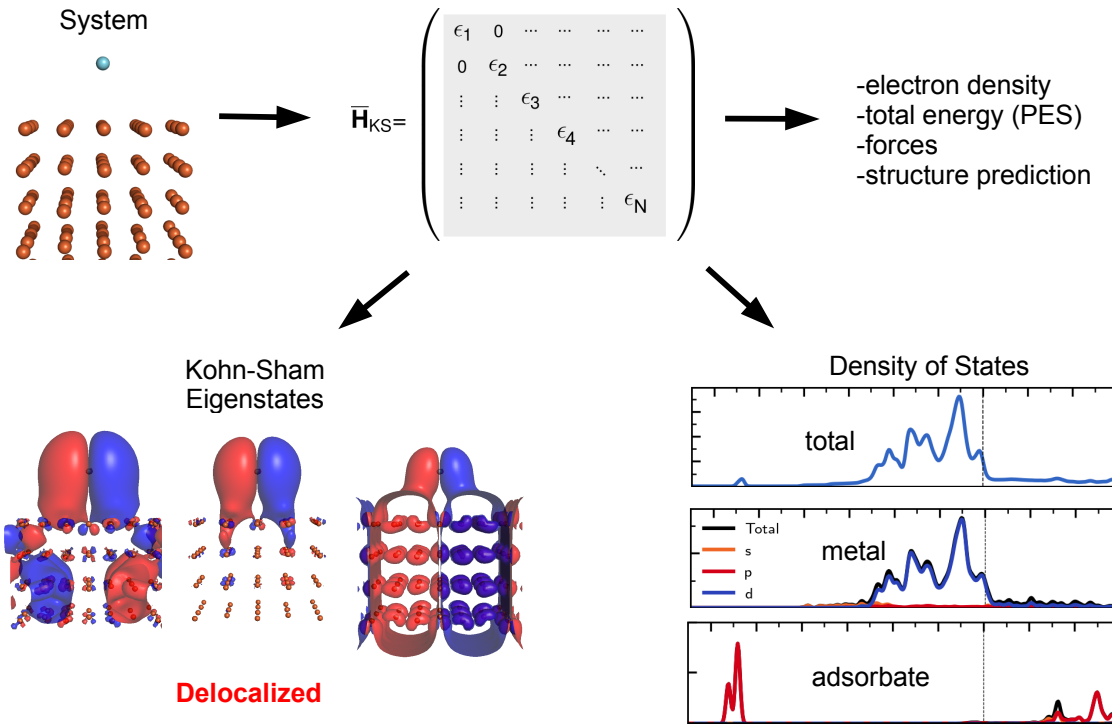
Localization Schemes

- Wannier, LMO (→ correlated methods)
- SPADE (→ QM/MM embedding)
- Diabatization (→ charge transfer)
- +U Projector functions

→ local properties
→ chemical insight

Non-unique, qualitative, non-convergent

Adiabatic Representation



[1] W. Kohn, L.J. Sham, Physical Review (1965) (71,000 citations)
[2] R. Mulliken, JCP (1955) (11,000 citations)

Electronic Coupling H_{ad}

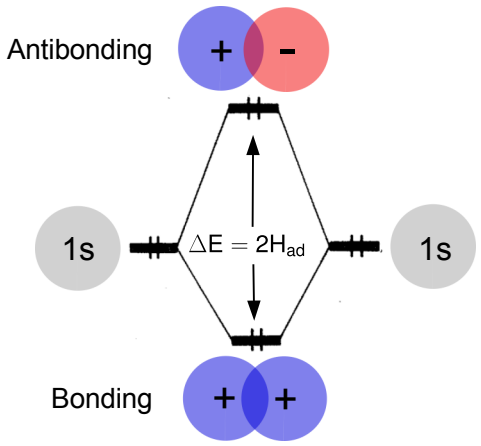
- A useful local property:
  - bonding, charge transfer
- a important *qualitative* descriptor
  - Not an observable
  - Not uniquely defined
  - Usually approximated

Coupling $H_{ad} = \langle \psi_a | \hat{H} | \psi_d \rangle$

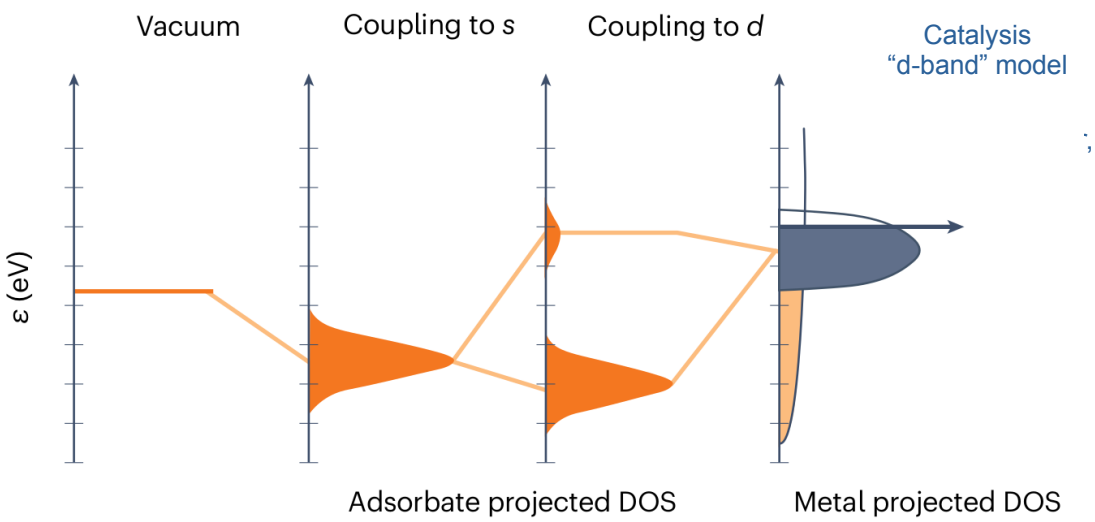
Overlap $S_{ad} = \langle \psi_a | \psi_a \rangle$

"Hopping term"
"Transfer integral"
"matrix element"

Molecules

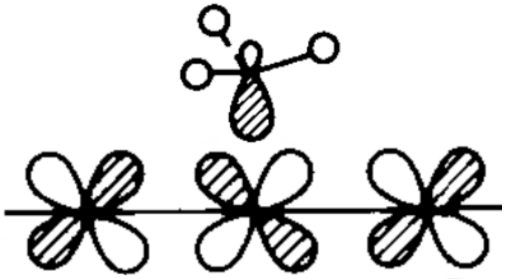


Surfaces

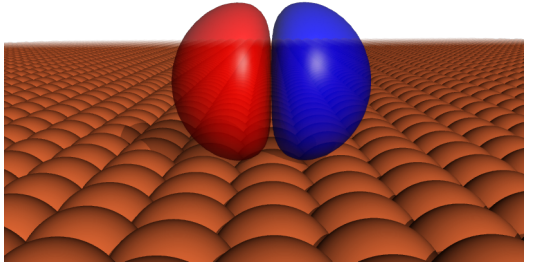


Mie Andersen, Nature Catalysis (2023).
J. Nørskov, B. Hammer, Surface Science (1995).

Can we calculate electronic coupling from DFT *quantitatively*?



Qualitative Model (1988)



$$H_{ad} = \langle \psi_a | \hat{H} | \psi_d \rangle$$

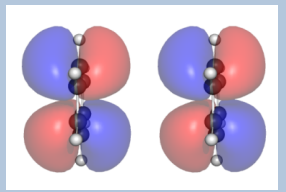
$$S_{ad} = \langle \psi_a | \psi_a \rangle$$

Quantitative Method (2023)

Outline

- A method to calculate electronic couplings quantitatively from DFT.

Molecules
Quantum chemical benchmarks



$H_{ad} = \langle \psi_a | \hat{H} | \psi_d \rangle$

Application

Validation

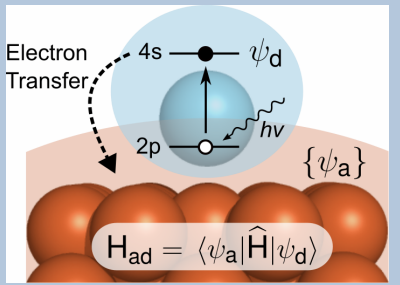
Electronic Coupling

Diabatization Method
bd_utils

DFT → H_{ad}

postprocessing

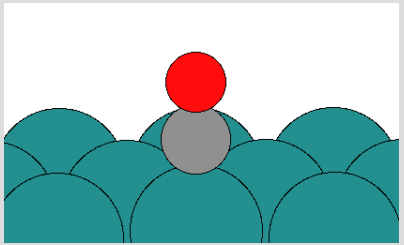
Surfaces
Ultrafast dynamics measurements



Atomic Probe Microscopy
AFM, STM, STS

Molecular Crystals
nanoelectronics

Catalysis
"The coupling to the d-band"



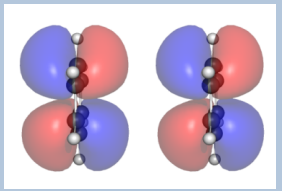
Highly Correlated Systems
(single-spin bits and qubits, Kondo effect)

Outline

- A method to calculate electronic couplings quantitatively from DFT.

Molecules

Quantum chemical benchmarks



$$H_{ad} = \langle \psi_a | \hat{H} | \psi_d \rangle$$

Application

Validation

Electronic Coupling

Diabatization Method

bd_utils

DFT $\longrightarrow$ H_{ad}

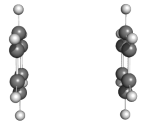
postprocessing

Calculating Electronic Coupling for Molecules

FHI-aims
The ab initio materials simulation package

output hamiltonian_matrix
output overlap_matrix

Benzene Dimer



acceptor donor

Diabatization

1) Run DFT
2) Project upon some localized states “diabats”
3) Read the couplings H_{ad}

Diabats are non-unique

Method	Diabatic States
Projection-Operator Diabatization (POD) [1]	**block eigenstates**
Fragment-orbital DFT (FODFT) [2]	isolated fragment MOs
Constrained DFT (CDFT) [3]	constrained adiabats

Projection-Operator Diabatization

Adiabatic Form

$$\overline{\mathbf{H}}_{KS}=\begin{pmatrix}\epsilon_1 & 0 & \cdots & \cdots & \cdots & \cdots \\ 0 & \epsilon_2 & \cdots & \cdots & \cdots & \cdots \\ \vdots & \vdots & \epsilon_3 & \cdots & \cdots & \cdots \\ \vdots & \vdots & \vdots & \epsilon_4 & \cdots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \epsilon_N \end{pmatrix}$$

$$\mathbf{H}_{KS}=\begin{pmatrix}\mathbf{H}_{aa} & \mathbf{H}_{ad} \\ \mathbf{H}_{da} & \mathbf{H}_{dd}\end{pmatrix}$$

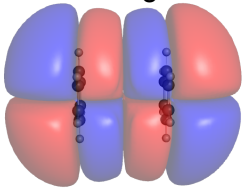
$$\mathbf{S}=\begin{pmatrix}\mathbf{S}_{aa} & \mathbf{S}_{ad} \\ \mathbf{S}_{da} & \mathbf{S}_{dd}\end{pmatrix}$$

Diabatic Form

$$\overline{\mathbf{H}}_{diag}=\begin{pmatrix}\epsilon_{a1} & 0 & \cdots & \overline{\mathbf{H}}_{ad} \\ 0 & \epsilon_{a2} & \cdots & \\ \vdots & \vdots & \ddots & \\ \overline{\mathbf{H}}_{ad} & & & \epsilon_{d1} \; 0 \; \cdots \\ & & & 0 \; \epsilon_{d2} \; \cdots \\ & & & \vdots \; \vdots \; \ddots \end{pmatrix}$$

Couplings!

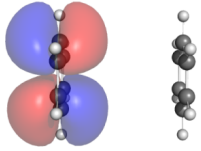
Kohn-Sham eigenstates

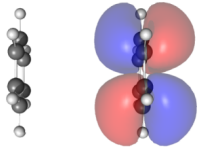


$|\psi_{KS}\rangle$ HOMO

Diabatic States

$|\psi_a\rangle$
HOMO





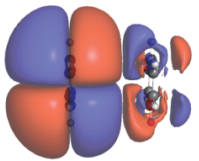
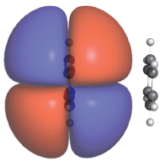
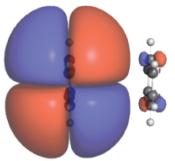
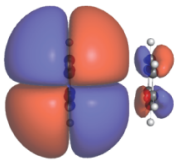
$|\psi_d\rangle$
HOMO

[1] I. Kondov, M. Thoss et al., Journal of Physical Chemistry C (2007)
[2] K. Senthilkumar, L. Siebbeles et al., Journal of Chemical Physics (2003)
[3] B. Kaduk, T. Van Voorhis et al., Chemical Reviews (2012)

Hab11 Benchmark [1]

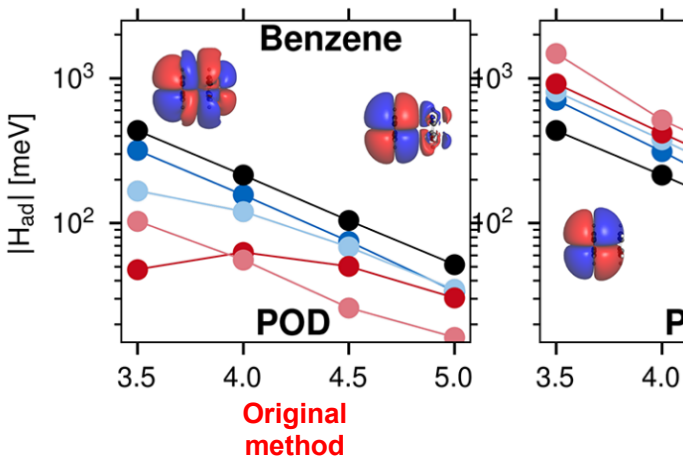
- **Problem:** original POD method **diverges** with basis set. [2]
- **Solution:** Improved Projection-Operator Diabatization methods. [3]
  - **POD2L, POD2GS: Accurate & Stable Couplings**

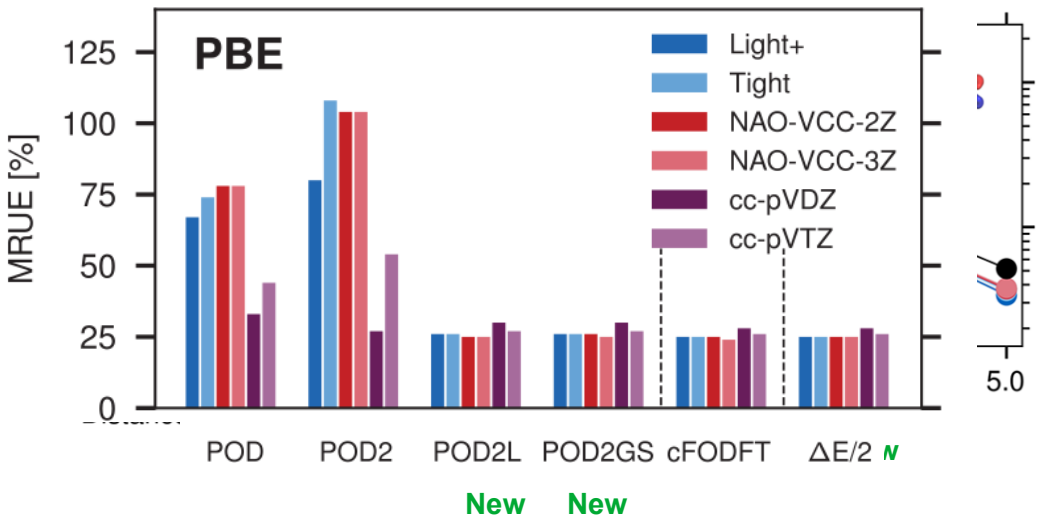
HOMO diabat, Benzene Dimer

	POD	POD2	POD2L	POD2GS
				
H_{ad}	34.8	72.5	36.4	36.4
	delocalized orthogonal	localized non-orthogonal	localized orthogonal (Löwdin) **New**	localized orthogonal (Gram-Schmidt) **New**

Ref: 51.7 meV

$H_{ad}(r)$ HOMO-HOMO Couplings, Error





[1] A. Kubas, H. Oberhofer, J. Blumberger et al., JCP (2014).
[2] I. Kondov, M. Thoss et al., Journal of Physical Chemistry C (2007)
[3] S. Ghan, C. Kunkel, K. Reuter and H. Oberhofer, JCTC (2020).

Outline

- A method to calculate electronic couplings quantitatively from DFT.

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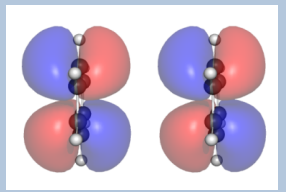
Quantum chemical benchmarks



$H_{ad} = \langle \psi_a | \hat{H} | \psi_d \rangle$

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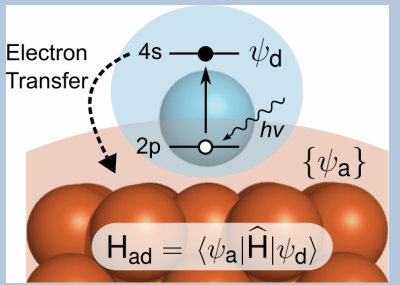
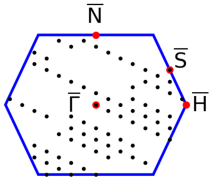
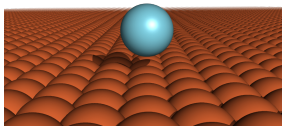


Calculating Coupling on (Periodic) Surfaces

FHI-aims
The ab initio materials simulation package





$$H_{ad,\mathbf{k}} = \langle \psi_{a,\mathbf{k}} | \widehat{H_{\mathbf{k}}} | \psi_{d,\mathbf{k}} \rangle$$

"What is the coupling of an adsorbate to the surface?"

Diabatization
in Periodic Boundary Conditions

1) Run DFT
2) Partition the Hamiltonian **(at each k-point)**
3) Project upon a local basis (diabats)
4) Read the couplings H_{ad}

Adiabatic Form

$$\overline{H}_{KS} = \begin{pmatrix} \epsilon_1 & 0 & \cdots & \cdots & \cdots & \cdots \\ 0 & \epsilon_2 & \cdots & \cdots & \cdots & \cdots \\ \vdots & \vdots & \epsilon_3 & \cdots & \cdots & \cdots \\ \vdots & \vdots & \vdots & \epsilon_4 & \cdots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \epsilon_N \end{pmatrix}$$

$$\mathbf{H}_{KS} = \begin{pmatrix} \mathbf{H}_{aa} & \mathbf{H}_{ad} \\ \mathbf{H}_{da} & \mathbf{H}_{dd} \end{pmatrix} \longrightarrow \mathbf{S} = \begin{pmatrix} \mathbf{S}_{aa} & \mathbf{S}_{ad} \\ \mathbf{S}_{da} & \mathbf{S}_{dd} \end{pmatrix}$$

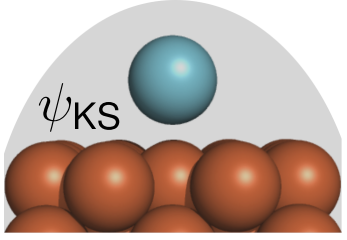
Diabatic Form

$$\overline{H}_{diag} = \begin{pmatrix} \epsilon_{a1} & \cdots & \cdots & \cdots & \overline{H}_{ad} \\ \vdots & \epsilon_{a2} & \cdots & \cdots & \\ \vdots & \vdots & \epsilon_{a3} & \cdots & \\ \vdots & \vdots & \vdots & \ddots & \\ \overline{H}_{ad} & & & & \epsilon_{d1} \; 0 \; \cdots \\ & & & & 0 \; \epsilon_{d2} \; \cdots \\ & & & & \vdots \; \vdots \; \ddots \end{pmatrix}$$

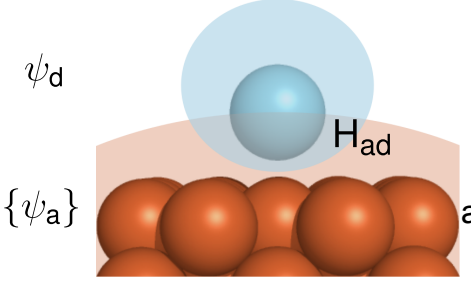
Couplings!

Diabatic states are non-unique

Method Name	Acceptor	Donor
($frag_a$,$POD2_d$)GS	clean surface adiabats	Block eigenstates
($frag_a$,$frag_d$)GS	clean surface adiabats	monolayer adiabats



Kohn-Sham eigenstates



How to Validate?

A first-principles Newns-Anderson Chemisorption Function

Newns-Anderson Model [1]

Chemisorption Functions:

Level shift: $$\Lambda(\epsilon) = \frac{P}{\pi}\int \frac{\Delta(\epsilon')}{\epsilon-\epsilon'}d\epsilon'$$

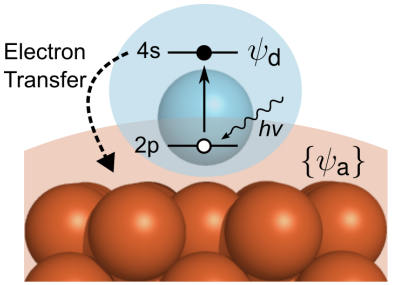
Line broadening: $$\Delta(\epsilon) = \pi\sum_{a}|H_{ad}|^2\delta(\epsilon-\epsilon_a)$$

First-principles **Method:**

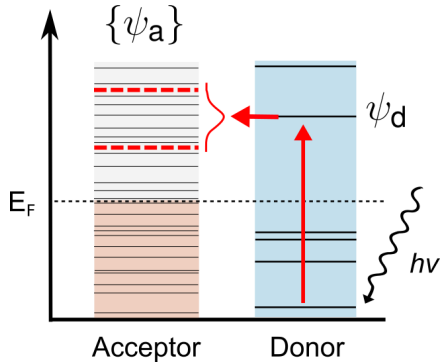
$$\Delta(\epsilon) = \frac{\pi}{\Omega_{BZ}}\int_{\Omega_{BZ}}\sum_{a}^{N}|H_{ad,\mathbf{k}}|^2 g_\sigma(\epsilon_{\mathbf{k}}-\epsilon_{a,\mathbf{k}})d\mathbf{k}$$

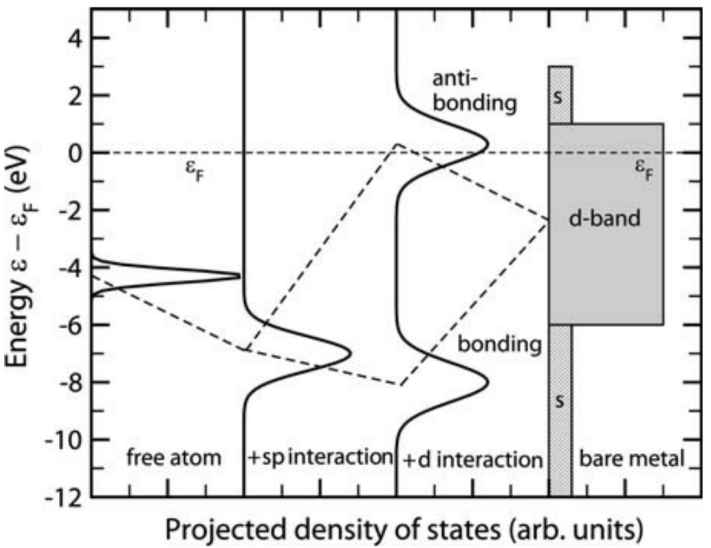
"coupling-weighted DOS"
"WDOS"

Electron Transfer Lifetime $$\tau_d = \frac{\hbar}{2\Delta(\epsilon_d)}$$



Core-hole-clock spectroscopy
Ar[4s*] / Transition Metal
Lifetime ~ 3 femtoseconds





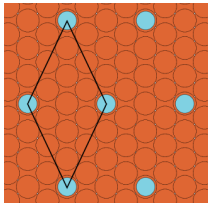
[1] D.M. Newns, *Self-Consistent Model of Hydrogen Chemisorption* Physical Review (1969) .

Axel Gross, *Theoretical Surface Science* (2009)

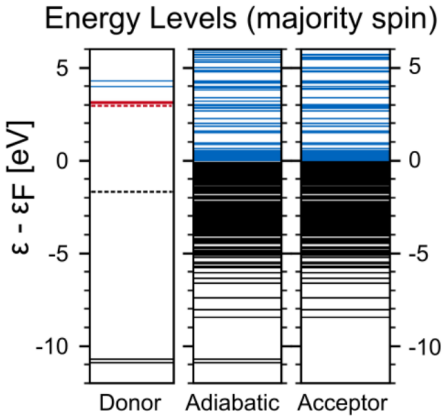
Electronic coupling of Argon 4s (LUMO) on Fe(110)

- Properties at **k=Γ**.

Ar@c(2x6)/Fe(110)

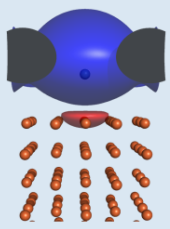


$\bar{H}_{KS}=$ $\begin{pmatrix} \epsilon_1 & 0 & \cdots & \cdots & \cdots & \cdots \\ 0 & \epsilon_2 & \cdots & \cdots & \cdots & \cdots \\ \vdots & \vdots & \epsilon_3 & \cdots & \cdots & \cdots \\ \vdots & \vdots & \vdots & \epsilon_4 & \cdots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \epsilon_N \end{pmatrix}$ → $\bar{H}_{diag}=$ $\begin{pmatrix} \epsilon_{a1} & \cdots & \cdots & \cdots & \bar{H}_{ad} \\ \vdots & \epsilon_{a2} & \cdots & \cdots & \\ \vdots & \vdots & \epsilon_{a3} & \cdots & \\ \vdots & \vdots & \vdots & \ddots & \\ \bar{H}_{ad} & & & & \epsilon_{d1}\ 0\ \cdots \\ & & & & 0\ \epsilon_{d2}\ \cdots \\ & & & & \vdots\ \vdots\ \ddots \end{pmatrix}$ →



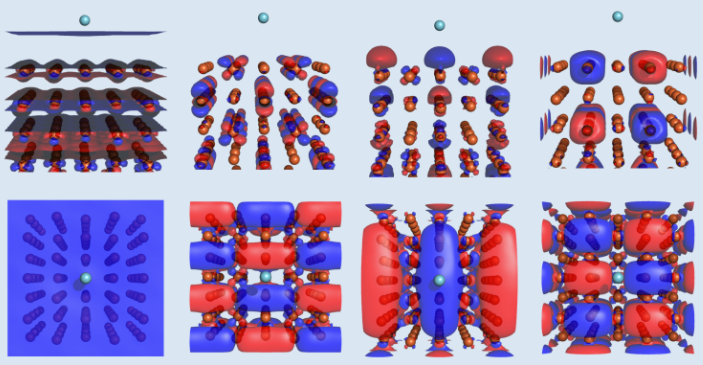
PBE+TSvdW
Light Tier 4 / 6-311+G**
4x4x1 kgrid
8 metal layers
Ar*[$2p_{3/2}^{-1}$4s] half core hole
force_occupation_projector

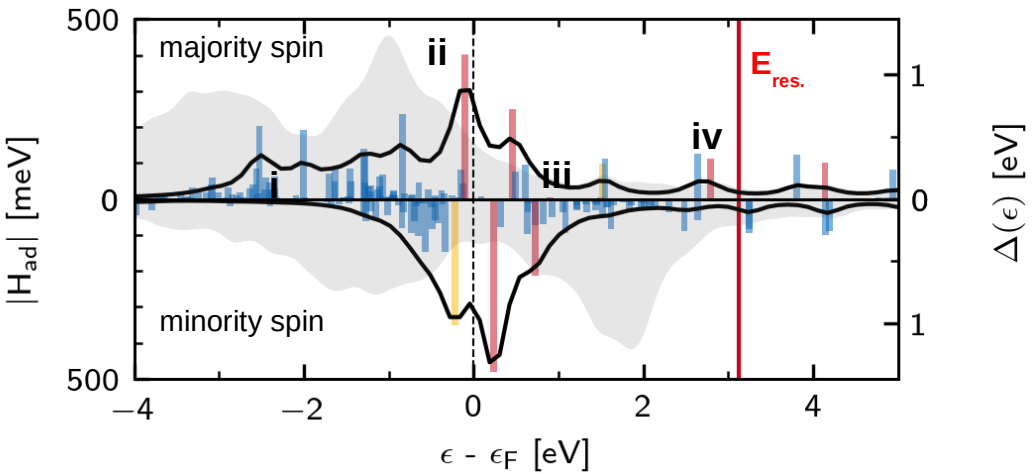
Donor



Character:
0.77 *s*, 0.22 p_z

Acceptor States



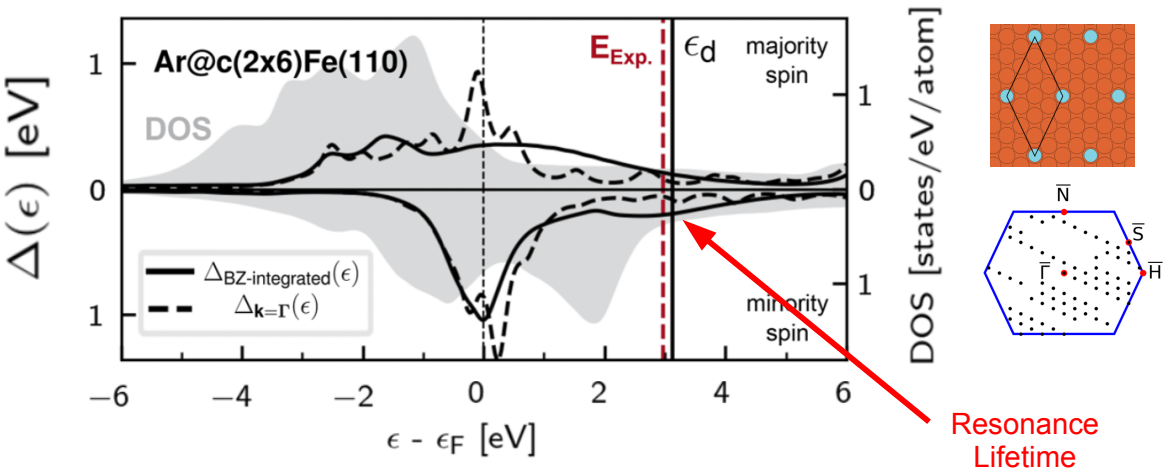


$$\Delta_{\mathbf{k}=\Gamma}(\epsilon) = \pi \sum_{a}^{N} |H_{ad,\mathbf{k}}|^2 g_\sigma(\epsilon_{\mathbf{k}} - \epsilon_{a,\mathbf{k}})$$

Chemisorption Function: Ar*[$2p_{3/2}^{-1}4s$] on Transition Metals

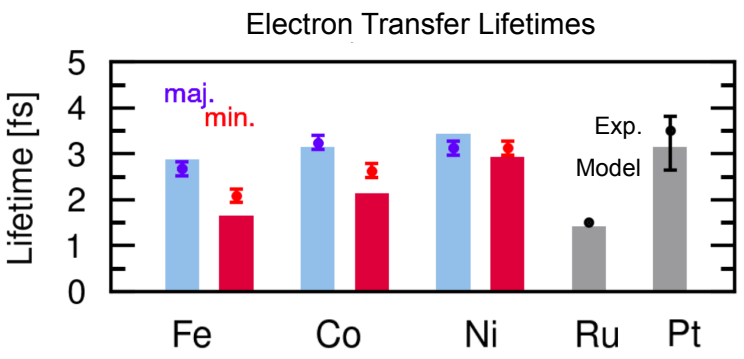
$$\Delta(\epsilon) = \frac{\pi}{\Omega_{BZ}} \int_{\Omega_{BZ}} \sum_a^N |H_{ad,\mathbf{k}}|^2 g_\sigma(\epsilon_\mathbf{k} - \epsilon_{a,\mathbf{k}}) d\mathbf{k}$$

- Brillouin Zone averaging: 12x12x1k

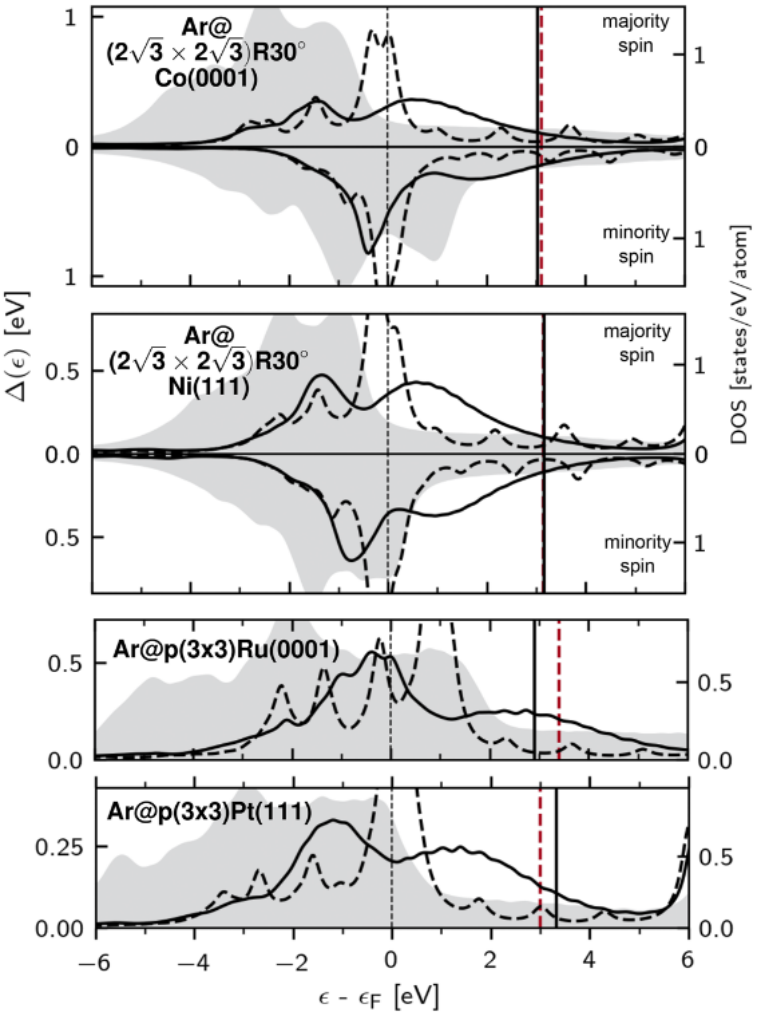


Resonance Lifetime Broadening

$$\tau_d = \frac{\hbar}{2\Delta(\epsilon_d)}$$



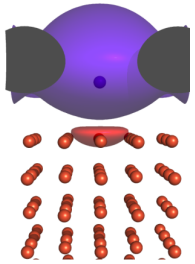
→ **Electronic Couplings are validated.**

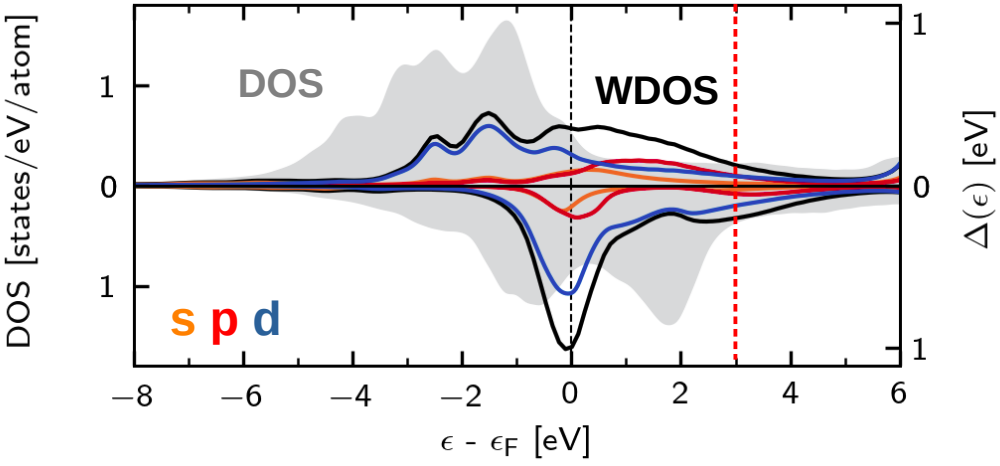


Ultrafast Core-hole-clock Measurements:
[1] Ar/Fe,Co,Ni Blobner, Han, Kim, Wurth and Feulner, PRL (2014).
[2] Ar/Ru Wurth, Menzel Chem. Phys. (2000).
[3] Ar/Pt Karis, Nilsson PRL (1996).

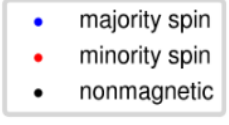
Interpretation

- "What is the coupling of the adsorbate to the surface bands?"
  - What is the role of the d-band?
- How important are **phase effects?**



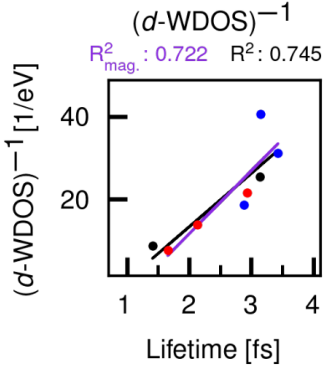


New insight: ET Lifetimes are determined by surface d-channel
-spin dependence
-surface dependence



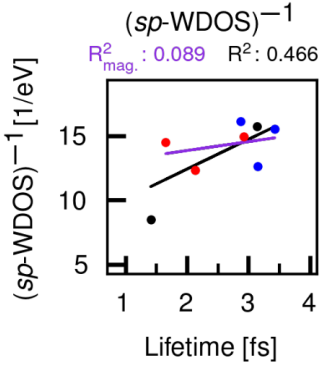
We can revisit coupling approximations in
1) STM
2) Catalysis

Analysis of Electron Transfer Lifetimes



New descriptor

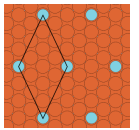
Trivial phase effect
(Tersoff-Hamann STM)
(d-band model, catalysis)

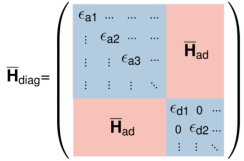


Old descriptor

non-trivial phase effect
(Chen's Derivative Rules, STM)

Role of Phase





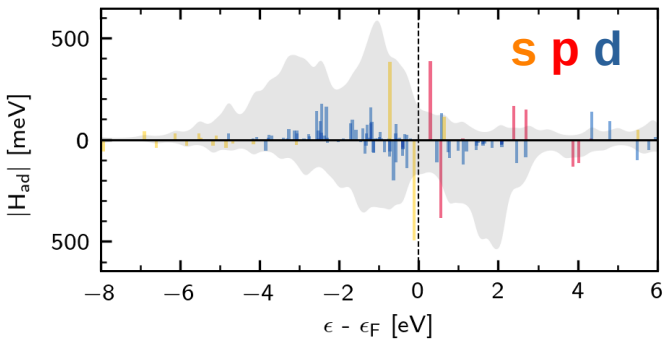
- Fragment versus POD2 diabats. ***Orbital hybridization affects couplings.***

Electronic Couplings, **k=Γ**.

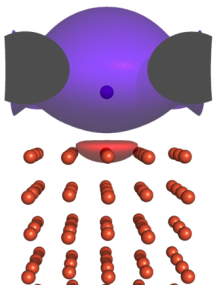
Donor State

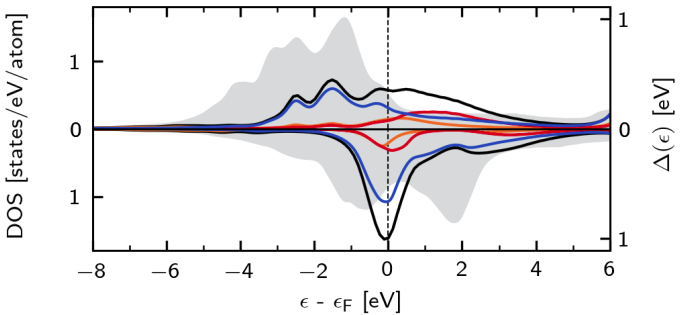
BZ-averaged Chemisorption Function, k12x12x1

($frag_a$,$POD2_d$)GS

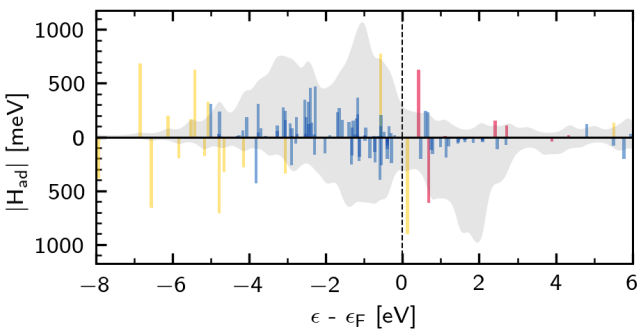


Unconstrained Ar4s4pz

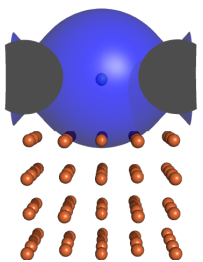


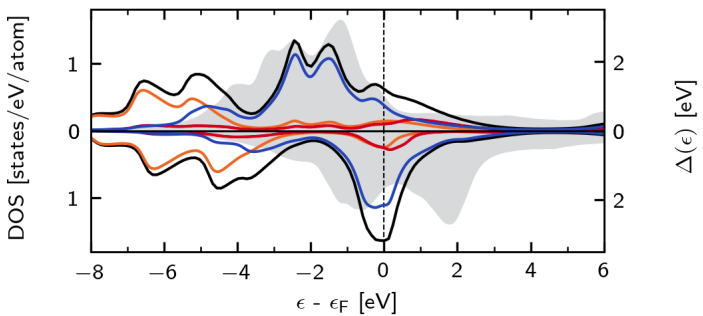


($frag_a$,$frag_d$)GS



Constrained Ar 4s

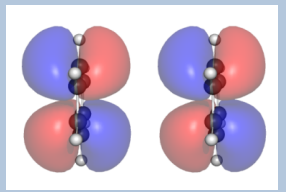




Outline

- A method to calculate electronic couplings quantitatively from DFT.

Molecules
Quantum chemical benchmarks



$H_{ad} = \langle \psi_a | \hat{H} | \psi_d \rangle$

Application

Validation

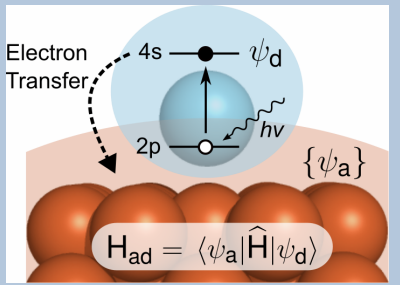
Electronic Coupling

Diabatization Method
bd_utils

DFT → H_{ad}

postprocessing

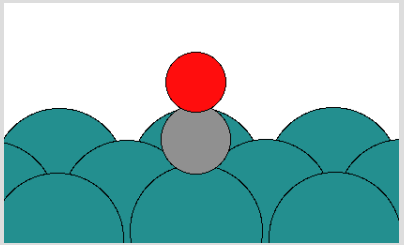
Surfaces
Ultrafast dynamics measurements



Molecular Crystals
nanoelectronics

Atomic Probe Microscopy
AFM, STM, STS

Catalysis
"The coupling to the d-band"



In Preparation

Your System Here?

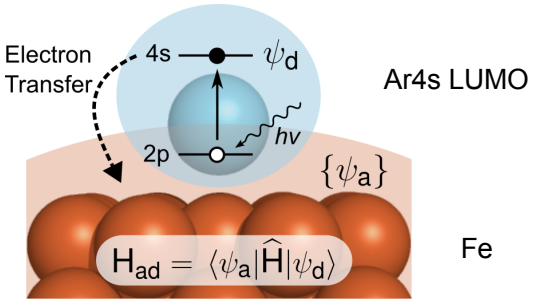
Highly Correlated Systems
(single-spin bits and qubits, Kondo effect)

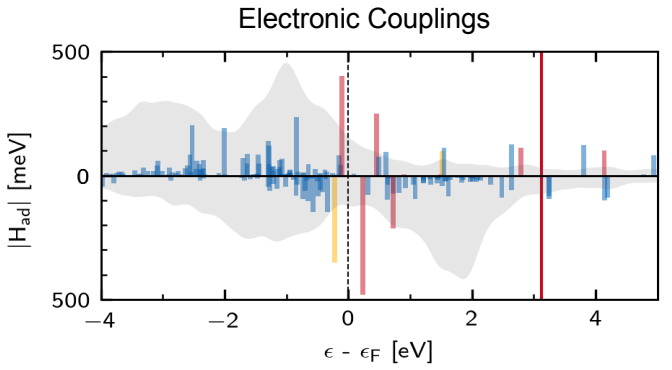
Conclusions

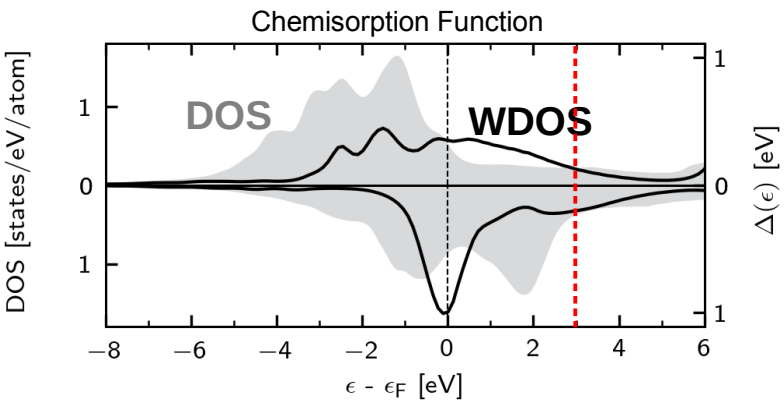
- We can calculate electronic coupling for molecules [1] and surfaces [2] from DFT.
- Couplings are accurate and highly interpretable.
  - **A new way to describe surfaces.**
- **Applications**
  - Ultrafast dynamics
  - Catalysis (d-band model)
  - STM / AFM
  - Highly Correlated systems (Kondo Physics)

Diabatization Method
bd_utils
DFT → H_{ad}
postprocessing

Collaboration Welcome





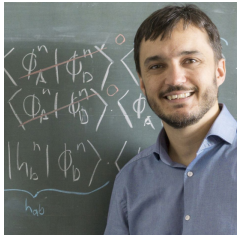


[1] *Improved Projection-Operator Diabatization Methods for the Calculation of Electronic Coupling Values*
S. Ghan, C. Kunkel, K. Reuter and H. Oberhofer, Journal of Chemical Theory and Computation (2020).

[2] *Interpreting Ultrafast Electron Transfer on Surfaces with a Converged First-principles Newns-Anderson Chemisorption Function*
S. Ghan, E. Diesen, C. Kunkel, K. Reuter and H. Oberhofer, Journal of Chemical Physics (2023) (Editor's Pick).

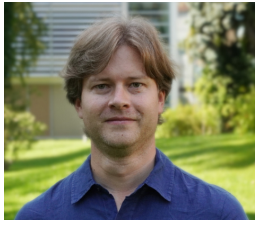
Thank You

Karsten Reuter (FHI)



Harald Oberhofer
(University of Bayreuth)

Christian Kunkel (FHI)



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FHI-aims
The ab initio materials simulation package

Georg Michelitsch
Christoph Schober