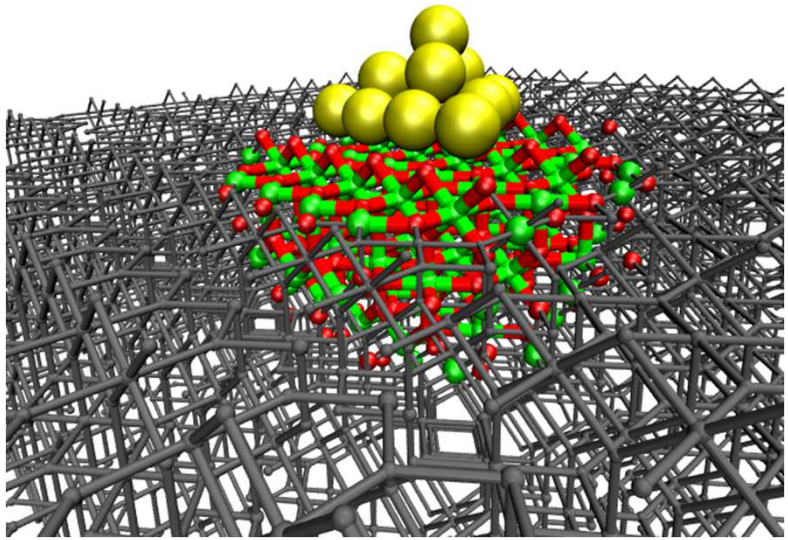
FHI-aims becomes embedded:
QM/Me and water splitting

Karsten Reuter

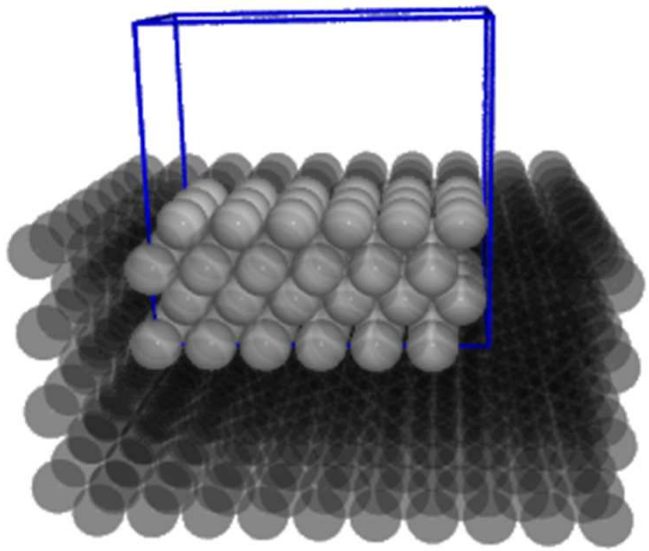
Chemistry Department and Catalysis Research Center
Technische Universität München

New features in FHI-aims

QM/MM



QM/Me



I. QM/MM:

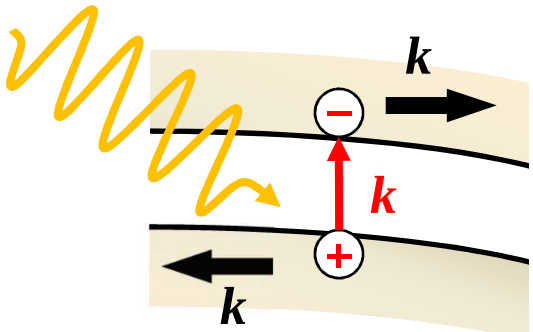
First-principles kinetic modeling for solar hydrogen production

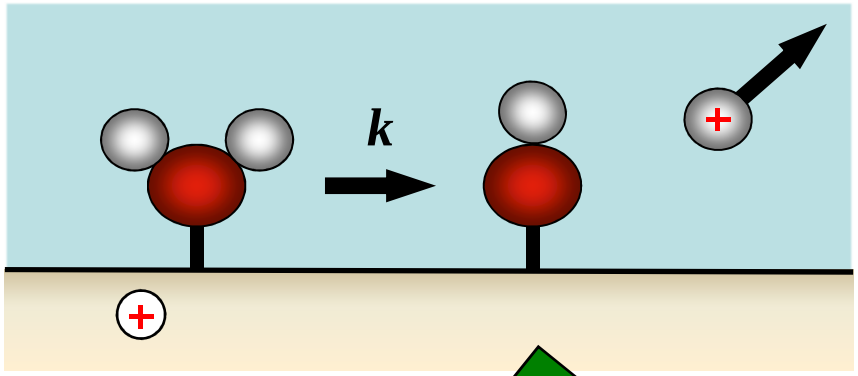
Daniel Berger

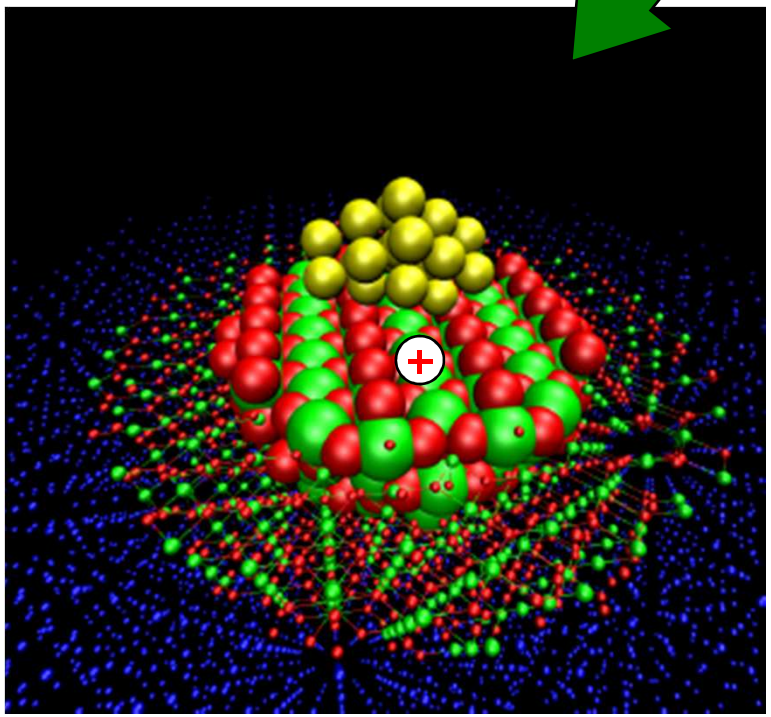
Harald Oberhofer

Volker Blum

Our approach to photoelectrochemistry







QM/MM:
FHI-Aims
meets
Chem-Shell

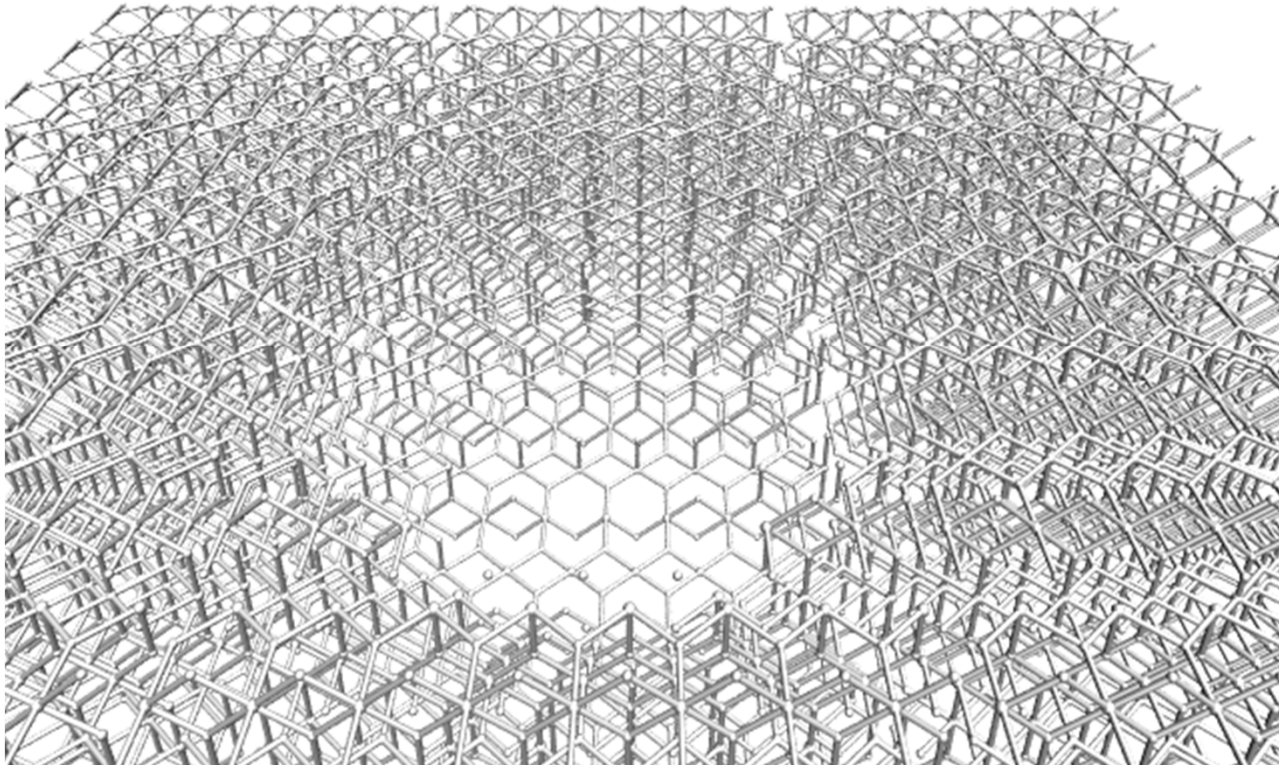
HPC-Europa2

with Andrew Logsdail
and Alexey Sokol

QM/MM and charge leakage

Covalent/non-ionic compounds:

- Spurious charge transfer out of QM zone
- Dangling bonds at cluster periphery



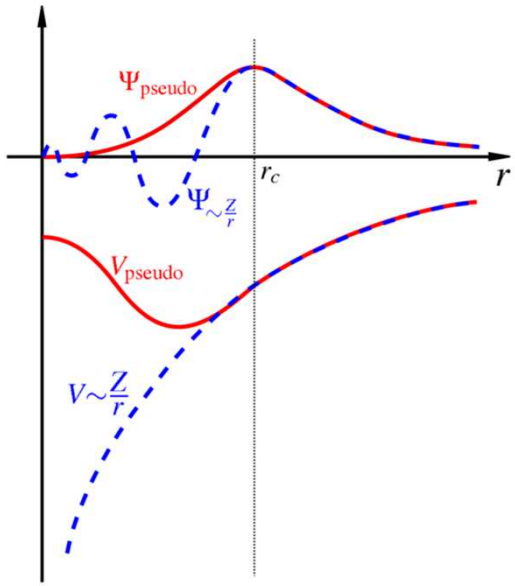
Finite QM cluster model:

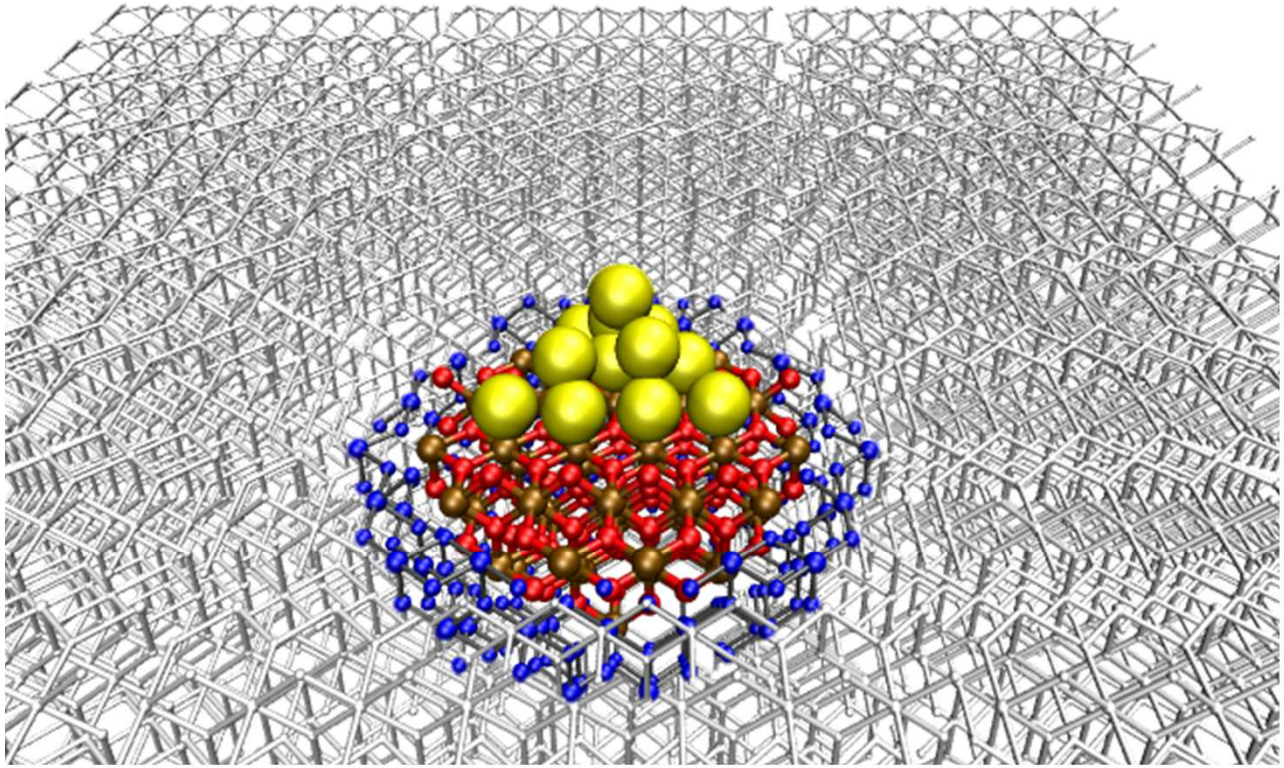
- Explicit electronic structure
- Bond making and breaking
- „First-principles“ accuracy

Extended MM region (here: multipoles):

- Correct electrostatics (here: Madelung potential)

Introducing a transition zone





Replace point charges at cluster periphery by pseudo-potentials

NCPPs in FHI-aims

Norm-conserving pseudopotentials in fully separable Kleinman-Bylander form:

$$\hat{V}^{KB} = \hat{V}_{loc}\delta(r - r') + \sum_{lm} |\chi^{KB}_{lm}\rangle E^{KB}_{l} \langle\chi^{KB}_{lm}|$$

M. Fuchs and M. Scheffler, Comp. Phys. Commun. 119, 67 (1999)
L. Kleinman and D.M. Bylander, Phys. Rev. Lett. 48, 1425 (1982)

Interaction with QM electrons:

$$E_{total} = E_{DFT} + \sum_{\alpha\beta} \hat{n}_{\alpha\beta} \langle\varphi_\alpha| \hat{V}_{KB} |\varphi_\beta\rangle$$

NAO

$$\langle\varphi_\alpha|\hat{V}^{KB}|\varphi_\beta\rangle = \langle\varphi_\alpha|\hat{V}_{loc}|\varphi_\beta\rangle + \sum_{lm}\langle\varphi_\alpha|\chi^{KB}_{lm}\rangle E^{KB}_{l}\langle\chi^{KB}_{lm}|\varphi_\beta\rangle$$

Local potential:

- Long-range
- Same for every electron
- Put on global integration grid

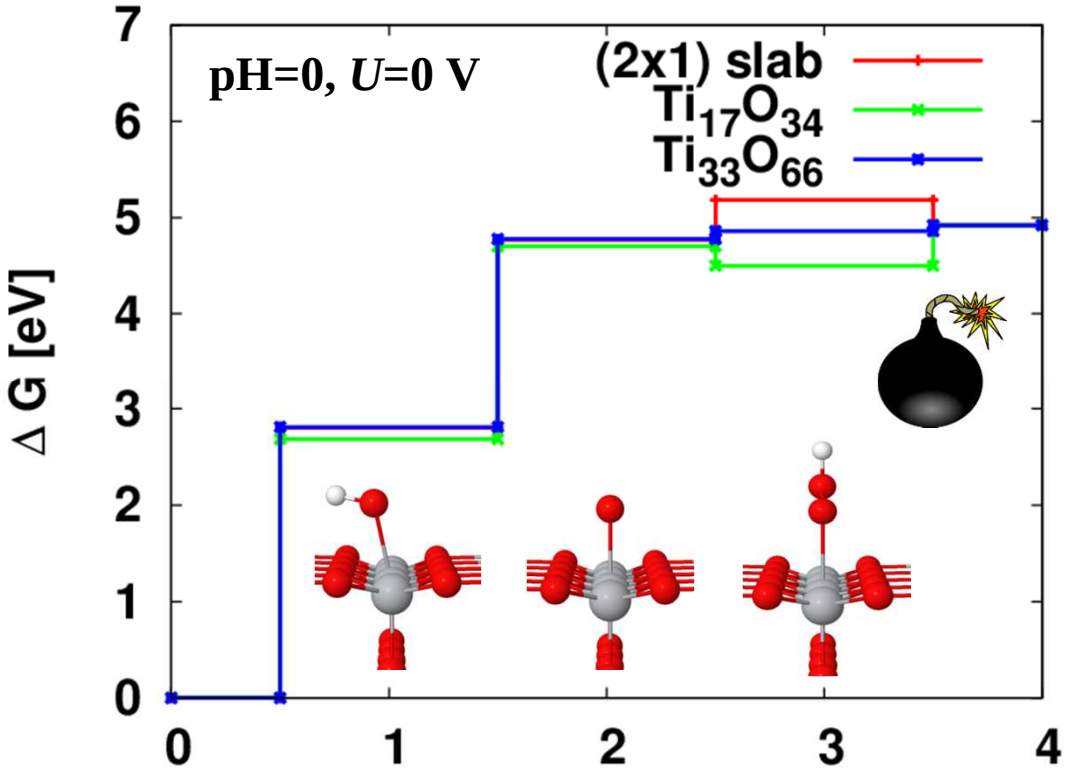
see poster by Daniel Berger

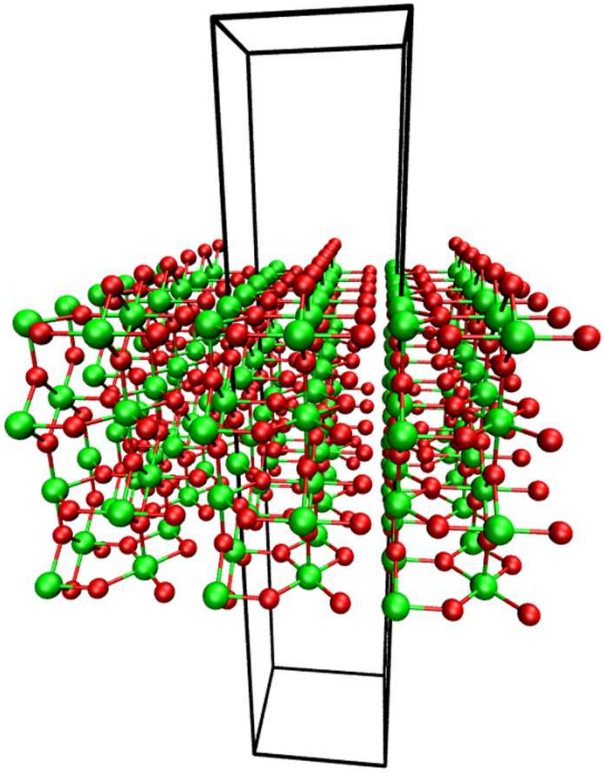
Non-local potential:

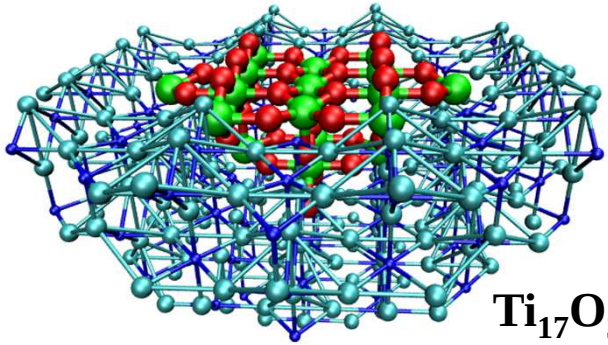
- Short-range
- Depends on angular momentum
- Compute and save (*n* x *m)* overlaps
- Efficient evaluation through spherical Bessel transformation

Benchmark: Water splitting at TiO_2(110)

- A: $H_2O + * \rightarrow HO* + H^+ + e^-$
- B: $HO* \rightarrow O* + H^+ + e^-$
- C: $H_2O + O* \rightarrow HOO* + H^+ + e^-$
- D: $HOO* \rightarrow O_2 + * + H^+ + e^-$







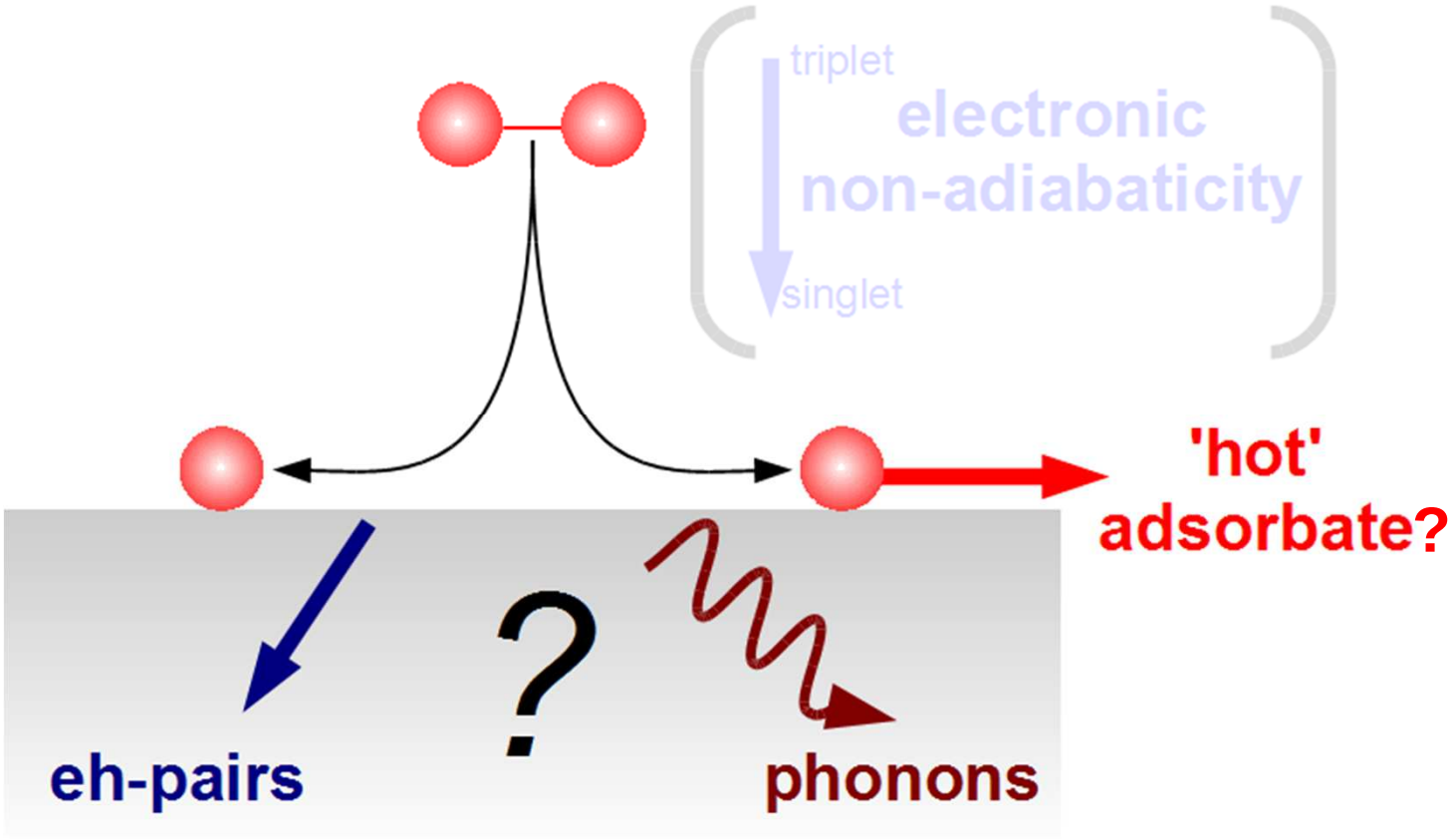
$Ti_{17}O_{34}$

II. QM/Me:

A novel embedding approach for adsorbate dynamics on metal surfaces

Jörg Meyer

Energy conversion at interfaces



Showcase O_2/Pd(100): **2.6eV adsorption energy released !**
(at GGA/PBE level)

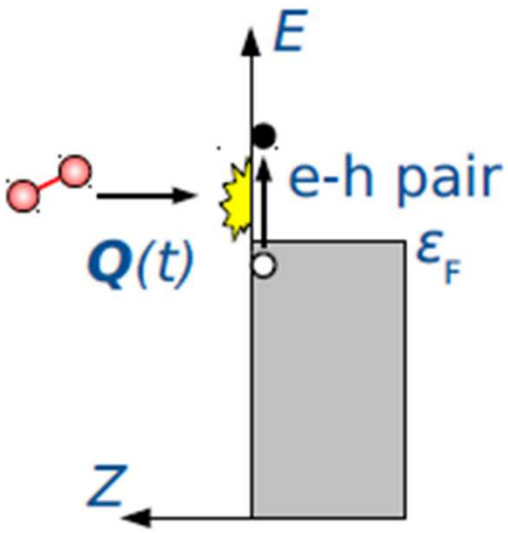
e-h pair excitation: Time-dependent perturbation theory

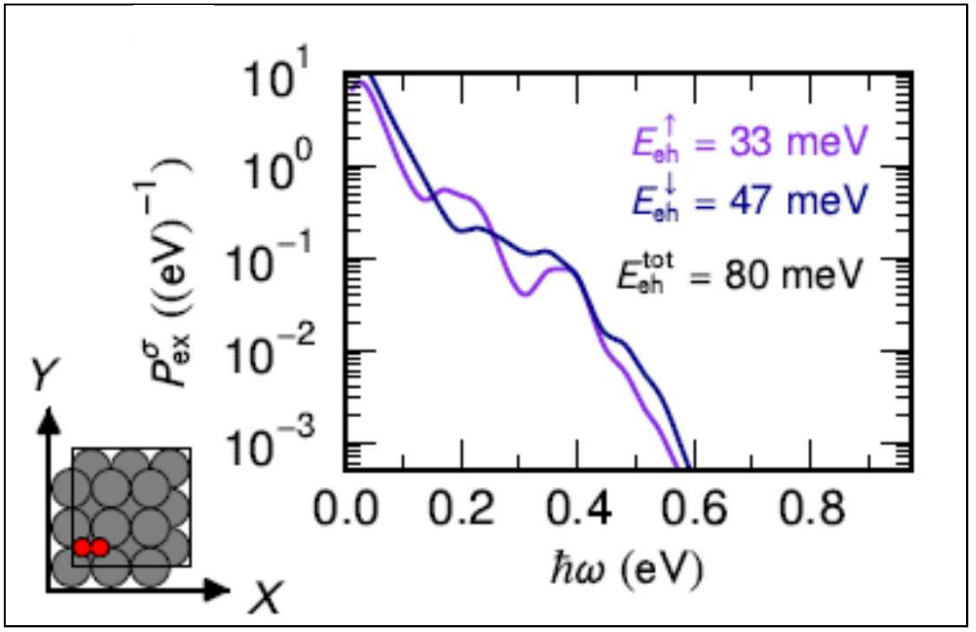
$$h^\sigma(t) \approx h_{(0)} + v^\sigma(Q(t))$$

M. Timmer and P. Kratzer,
Phys. Rev. B 79, 165407 (2009)

$$p_{ij}^\sigma(t) = \frac{1}{i\hbar}\,\langle \varepsilon_j^\sigma | v^\sigma(Q(t)) | \varepsilon_i^\sigma \rangle\, \exp\left(\frac{i}{\hbar}(\varepsilon_j^\sigma - \varepsilon_i^\sigma)\,t\right)$$

$$\tilde{P}_{\mathrm{ex}}^\sigma(\hbar\omega) = \sum_{ij} \left| \int_{-\infty}^{+\infty} \mathrm{d}t\; p_{ij}(t) \right|^2 \delta\left(\hbar\omega - (\varepsilon_j^\sigma - \varepsilon_i^\sigma)\right) \qquad E_{\mathrm{eh}}^\sigma = \int_0^{+\infty} \mathrm{d}\varepsilon\; \varepsilon\, P_{\mathrm{ex}}^\sigma(\varepsilon)$$





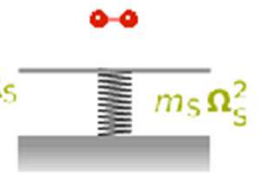
J. Meyer
and
K. Reuter,
New J. Phys.
13, 085010 (2011)

Phonon energy sinks „from the shelf“

- surface oscillator (SO) J. C. Polanyi and R. J. Wolf, *J. Chem. Phys.* **82**, 1555 (1985).

☺ easily coupled to frozen surface potential: $V_{6D}^{SO} = V_{6D}(\mathbf{R}_{6D} - \mathbf{R}_S) + \frac{1}{2} m_S \mathbf{R}_S \Omega_S^2 \mathbf{R}_S$

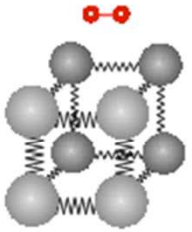
☹ minimalistic Einstein approximation for substrate degrees of freedom



- generalized Langevin equations J. C. Tully, *J. Chem. Phys.* **73**, 1975 (1980).

☺ in principle large bath included in ansatz: $H = H_{bath} + H_{sys} + H_{int}$

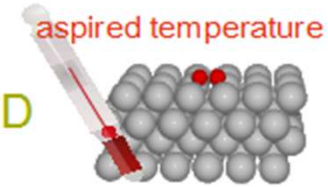
☹ ***but:*** in practice harmonic solid **and** approximations when integrating out bath degrees of freedom



- thermostats e.g. M. E. Tuckerman and G. J. Martyna, *J. Phys. Chem. B* **104**, 159 (2000).

☺ modified EOM allowing to sample ***NVT*** statistical properties via MD

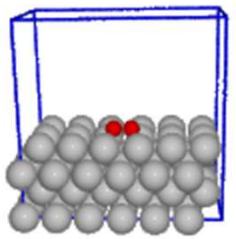
☹ ***but:*** single trajectories lose physical meaning



- *ab-initio* MD (AIMD) e.g. A. Groß, *Phys. Rev. Lett.* **103**, 246101 (2009).

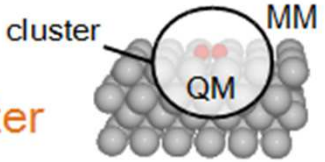
☺ substrate mobility described at *ab-initio* quality

☹ affordable supercell sizes (**PBC**s!) limits description of phonons

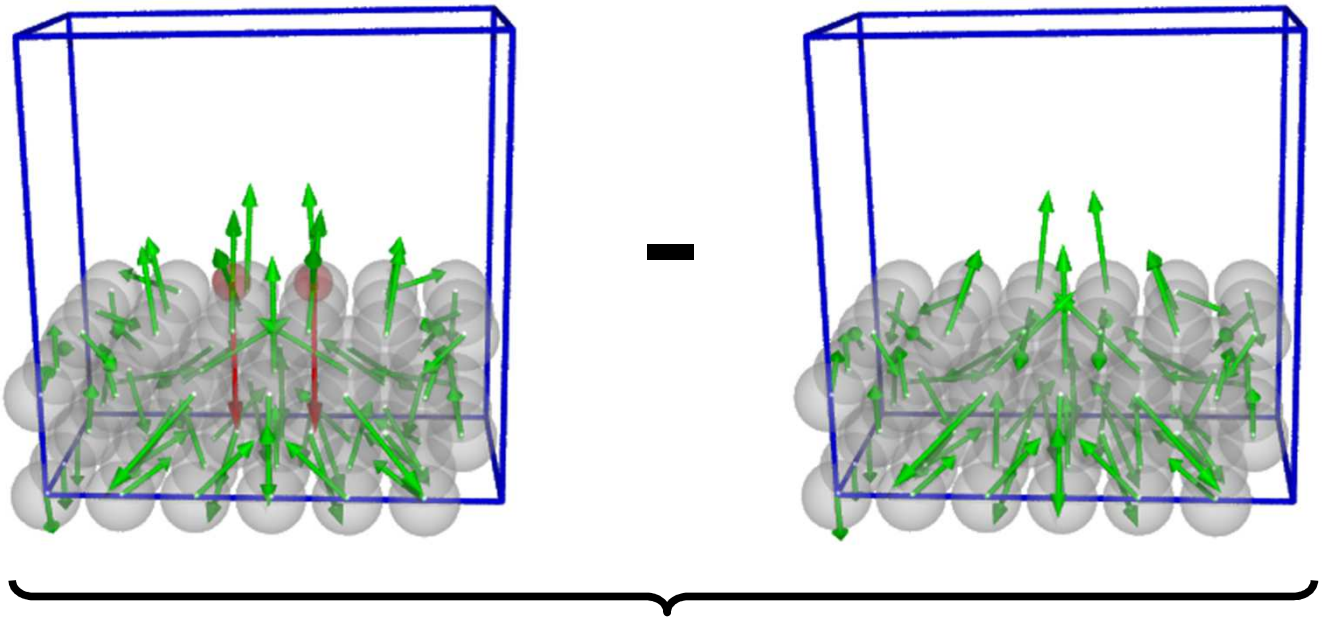


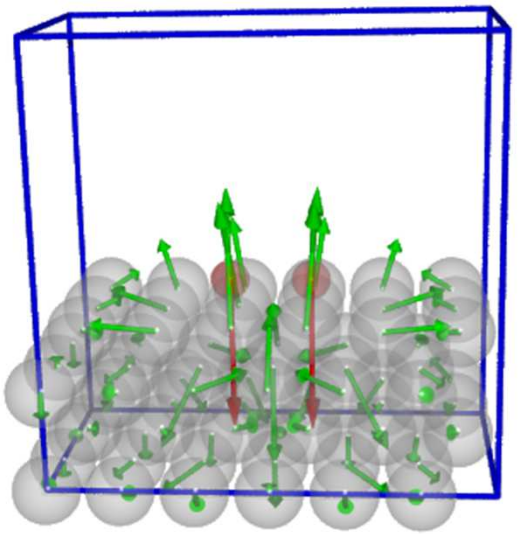
- QM/MM embedding e.g. C. Bo and F. Maseras, *Dalton Trans.* **2911** (2008).

☹ metallic band structure cannot be mimicked by feasibly large cluster



Exploiting locality: Elastic vs. chemical forces





Adsorbate-induced forces very short ranged !

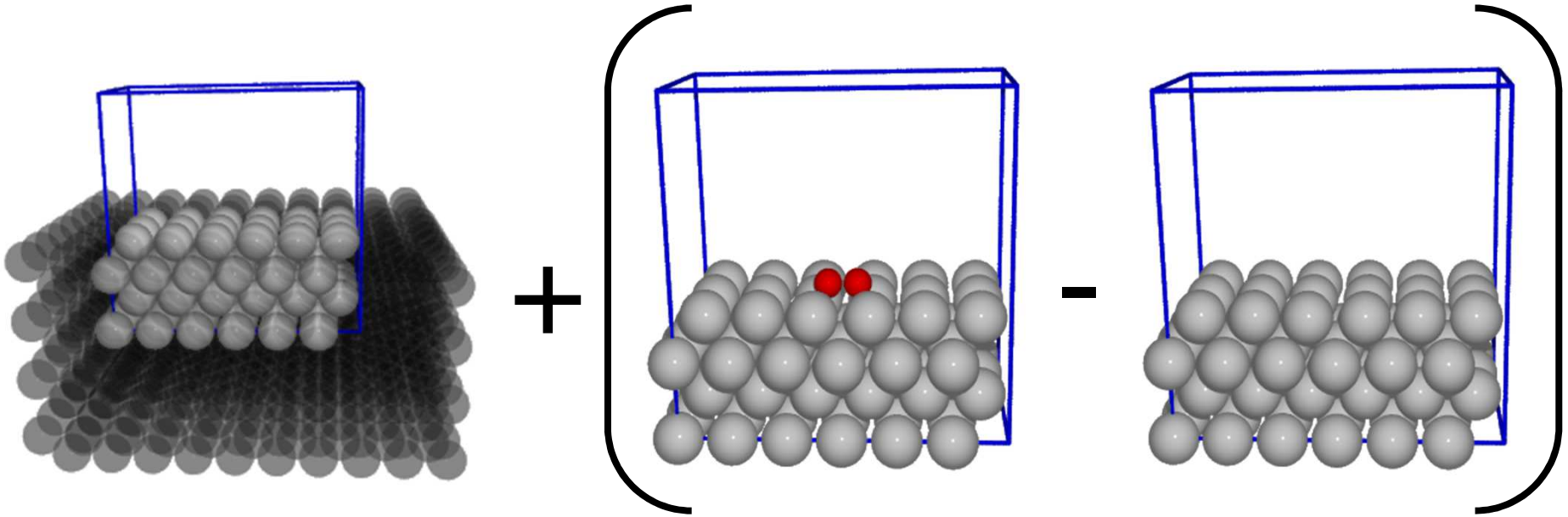
forces (eV/Å)

1.0

0.1

0.01

QM/Me embedding

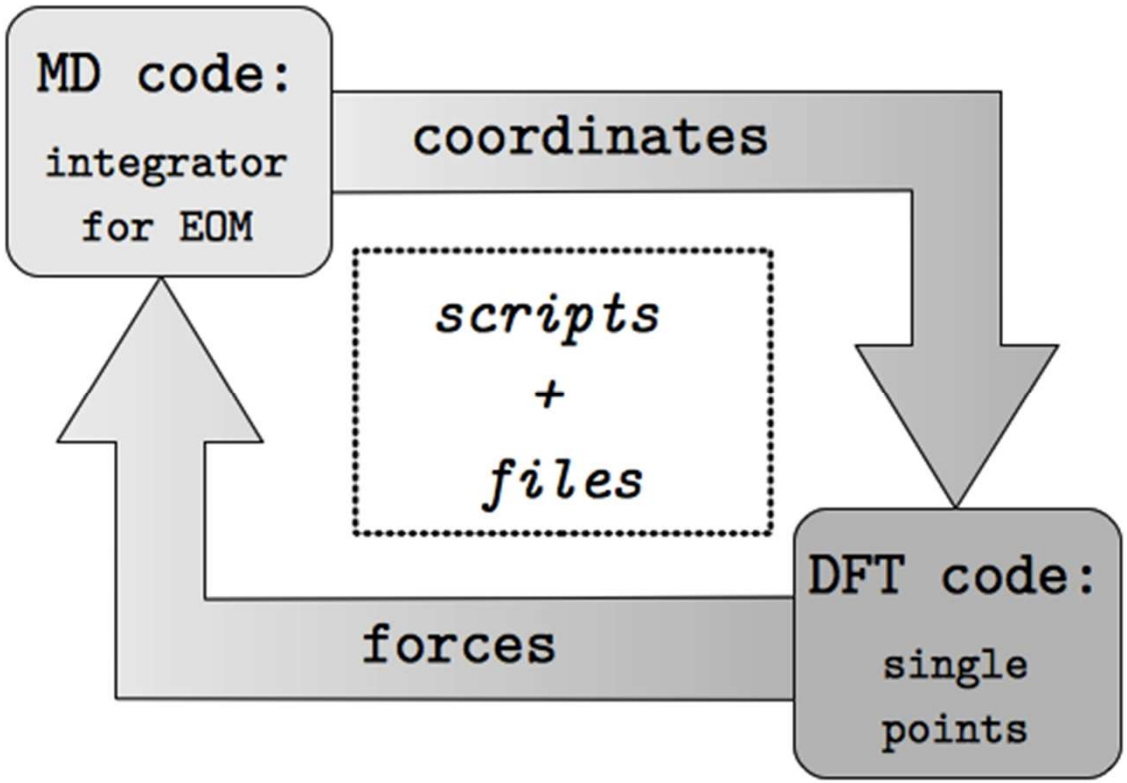


Large-scale MM MD … with additional QM-force contributions

DFT-parametrized MEAM
50x50x50 Pd atoms
LAMMPS
S. J. Plimpton, J. Comp. Phys. 117, 1 (1995)

DFT GGA/PBE
6x3x4 (or 8x3x4) slabs
CASTEP
S.J. Clark *et al.*, Z. Kristallogr. 220, 567 (2005)

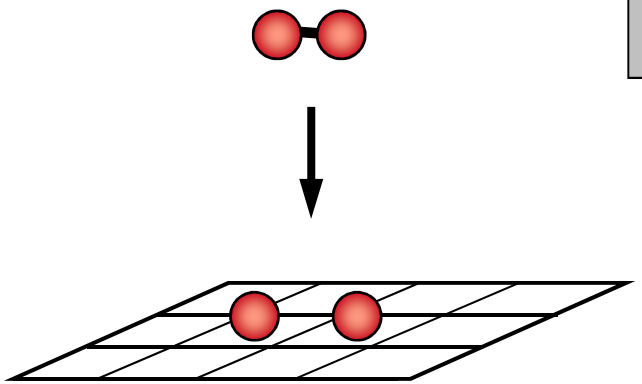
QM/Me in FHI-aims

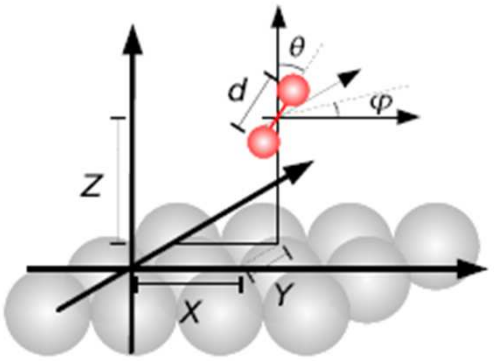


talk to Jörg Meyer (tutorial on Tuesday)

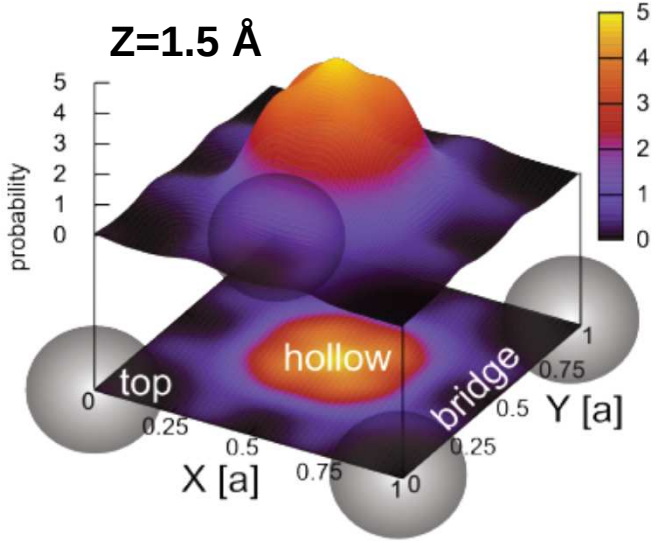
Forget Markov: Hot adatoms are alive!

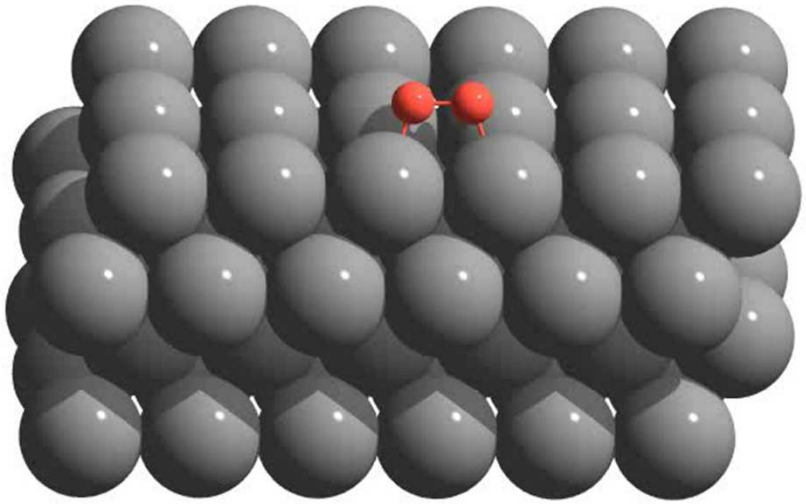
$$k = \tilde{S}_{\circ}(T)\frac{pA_{uc}}{\sqrt{2\pi m k_B T}}$$





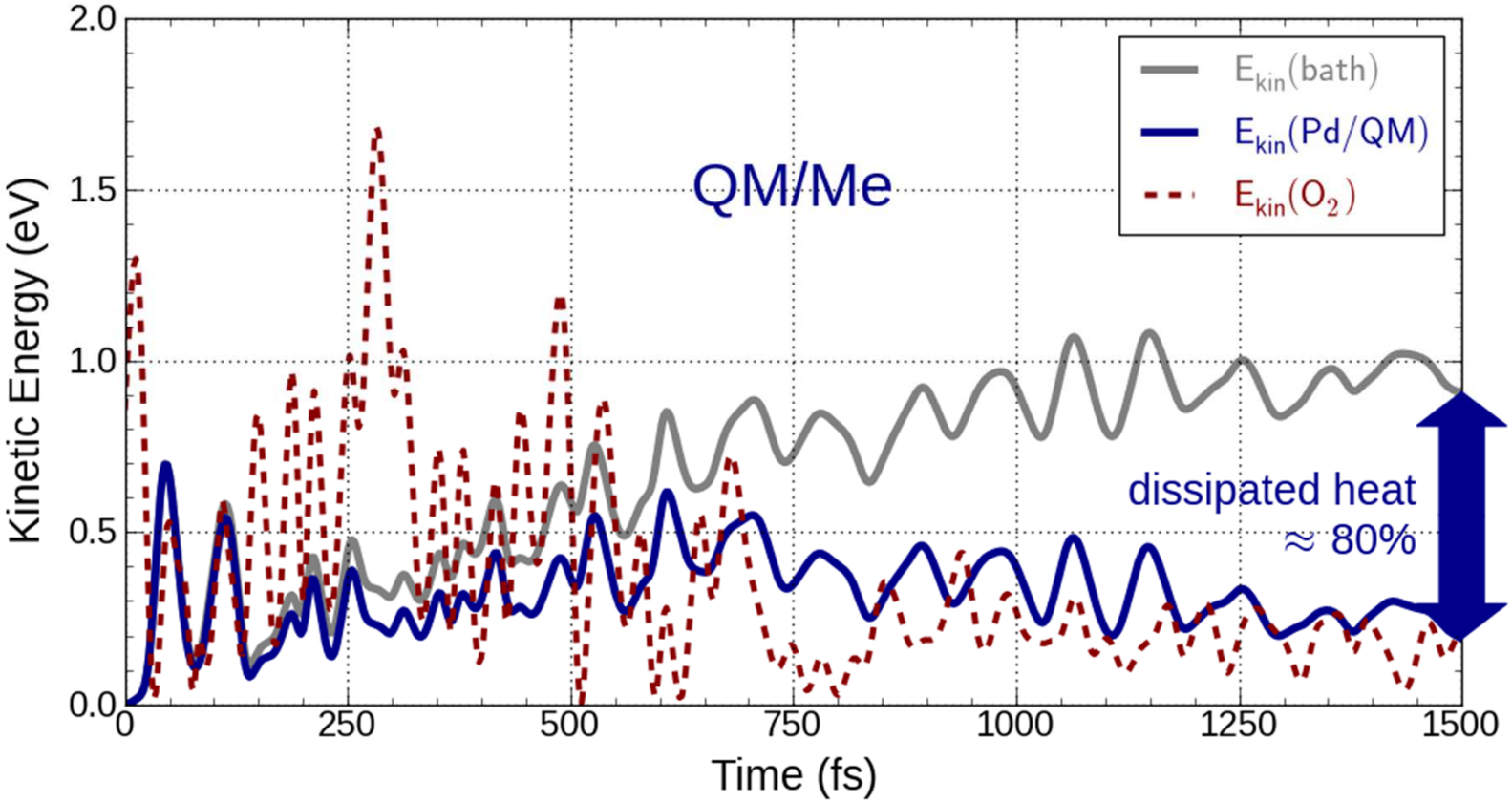
$V_{fsa} = (X, Y, Z, d, \theta, \varphi)$





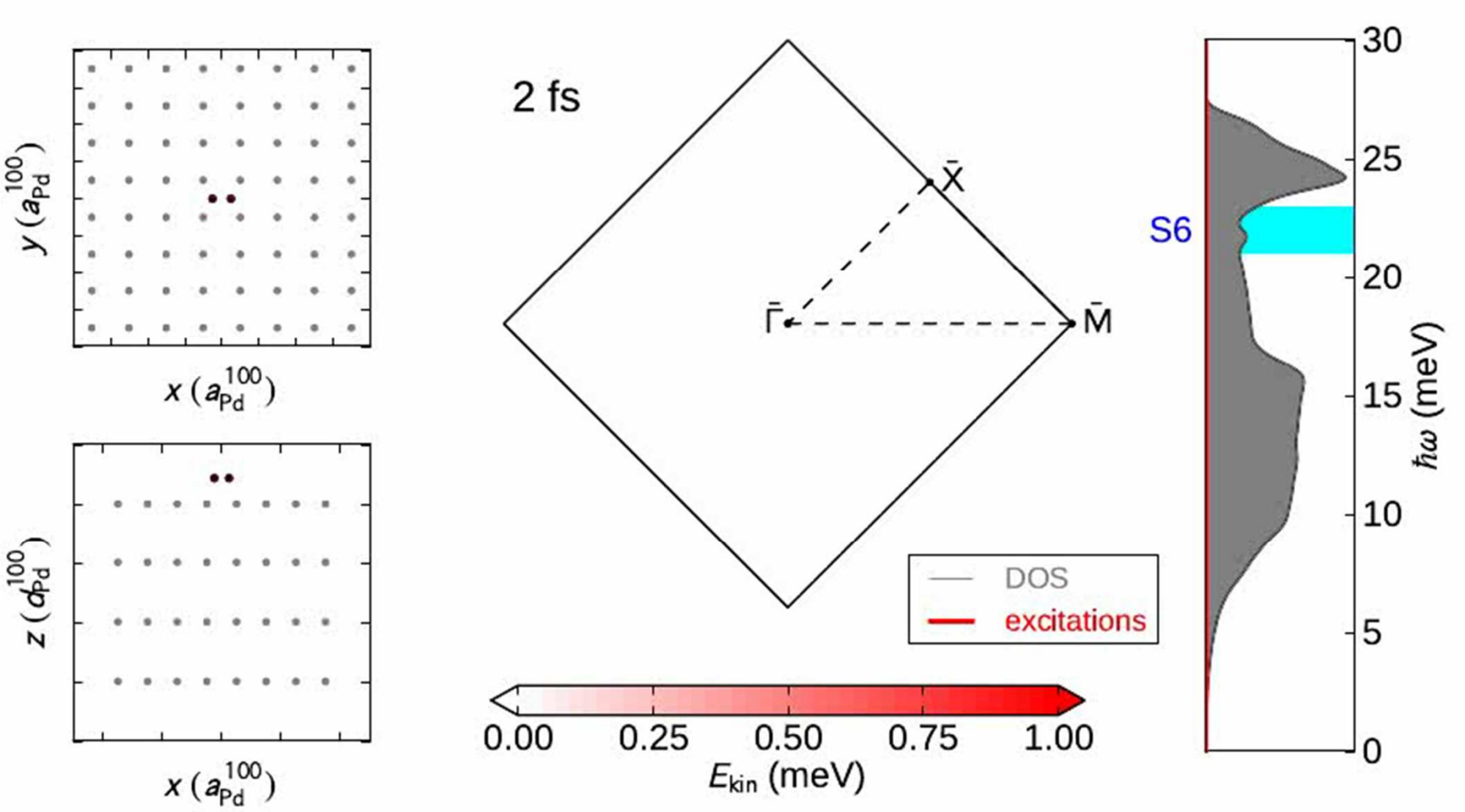
J. Meyer and K. Reuter, in preparation

Energy dissipation out of QM region



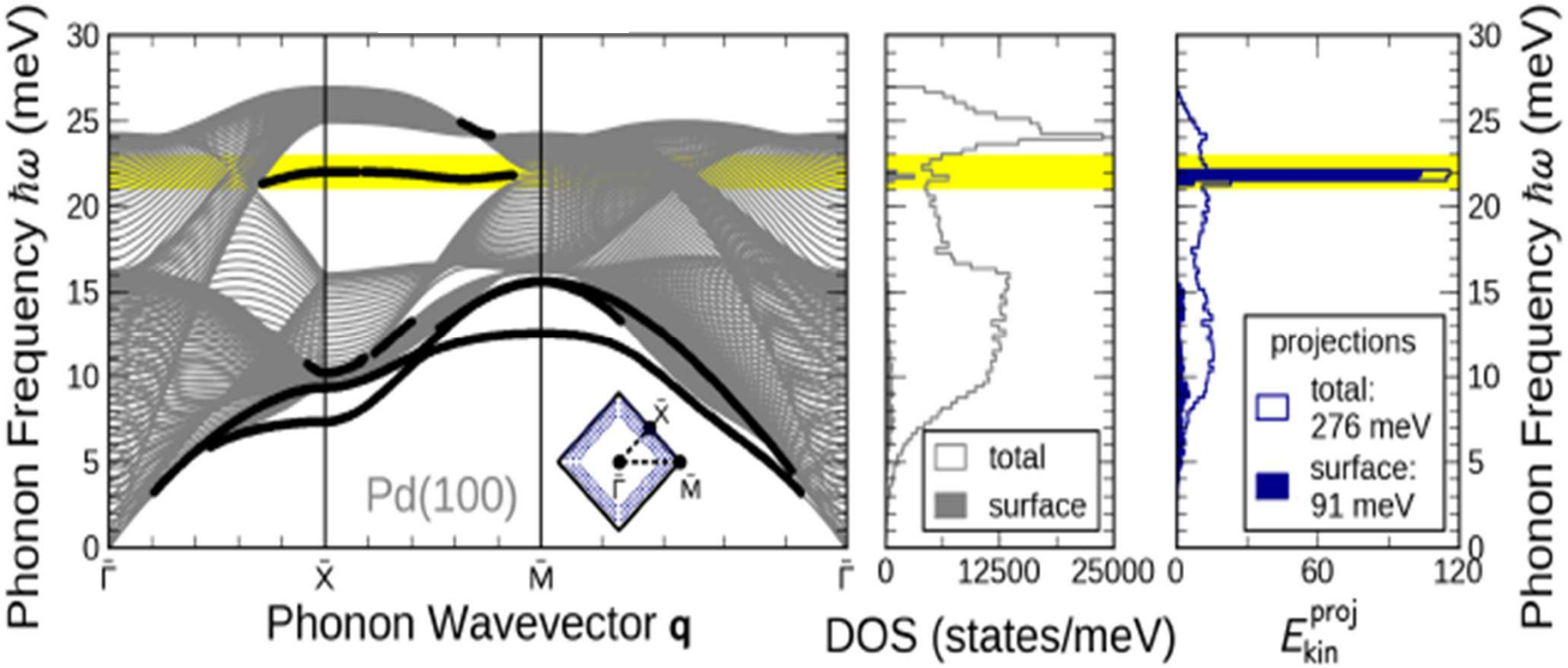
Dominant fraction of released energy is dissipated out of QM-region on picosecond timescale

Watching phonons getting all excited…



The role of surface phonons

t = 200 fs



Strong non-equilibrium population of non-Rayleigh surface phonon modes

J. Meyer and K. Reuter, in preparation

IGSSE TUM
International Graduate School of Science and Engineering

DFG

Alexander von Humboldt
Stiftung / Foundation

Thanks so much!!!

www.th4.ch.tum.de