

MC 3.1.8 Theoretische Chemie/ Quantenchemie Computerübungen im Wintersemester 2019/2020

Übung 10: QM/MM Methodology for Adsorbates on Metallic Interfaces

1 Introduction

In this exercise we are going to describe a porphyrine molecule adsorbed on a gold surface. Systems like this are often used in Tip Enhanced Raman Spectroscopy experiments, but adsorbate interface systems also have many applications closer to material sciences. Applications include zeolites as molecular sieves, functionalized surfaces with molecular monolayer adsorbates, such as graphene, nanobiotechnology, description of lattice defects and many more.

Often it is not possible to easily isolate a small model system without sacrificing accuracy and crucial interactions. On the other hand, description of the full system with high accuracy methods is often too expensive. A hybrid method, that originally came from the biochemistry community, has combined applications of quantum mechanical and molecular mechanical methods, so called QM/MM methods [12, 11].

1.1 Image Charge QM/MM

The Image-Charge QM/MM method is a comparably new development, especially targeted at the description of adsorbates on metallic surfaces. [2] The two most common versions of QM/MM methods are mechanical and electrostatic embedding. In the former the only coupling between the QM and MM part of the system, is by constraints in atomic positions at the QM and MM boundaries, so that only forces couple, while for the latter the QM part is polarized by the MM point charges and possibly vice versa. [6]

The IC-QM/MM methods extends the concept of electrostatic embedding, and allows the electrostatic potential, generated by the QM part, to induce a response in the MM part. Spherical Gaussians are centred at the MM atoms, representing smeared charges. These are optimized to self consistency together with the wave function of the QM part. The advantage of this method, compared to normal electrostatic embedding, is, that in the case of metallic surfaces, such as gold, where all the charges are 0, correct polarization of the wavefunction can still occur and no physically meaningless results in properties, such as the electrostatic potential, will be obtained. [2]

2 Calculation Details

We use *CP2K* [5] to calculate the infrared spectrum and the electrostatic potential of porphyrine in the gas phase and adsorbed to a gold surface as well as the adsorption energy. For computational efficiency this is done using the IC-QM/MM method, which is available in *CP2K*. To do so, we need calculations on three different systems: isolated porphyrine, a gold surface and porphyrine attached to a gold surface.

2.1 Porphyrine

Use *Avogadro* [4] to get the porphyrine structure (use "File> Import from chemical name or draw by hand and optimize) and save the structure as PDB file. Make sure, to change the atomic labels of the nitrogen atoms to N2 or N3, respectively, depending on whether the nitrogen atom is sp^2 or sp^3 hybridized. While this does not matter for a pure quantum calculation, it will be relevant for subsequent steps.

This time, we use the TPSS0 functional (TPSS [10] with 25% Hartree-Fock exchange), which is a meta hybrid functional, so we need to calculate Hartree-Fock exchange terms. This is a two-step procedure in CP2K: first, a converged wavefunction for the corresponding GGA needs to be calculated, which is then used as an initial guess for the hybrid DFT calculation. Therefore, for our initial geometry we do a single point calculation with the TPSS functional and the same cell size as in the IC-QM/MM calculation, in order to be able to compare energies.

Listing 1: *CP2K* input file for a single point energy calculation using the TPSS functional. A wavefunction file, which is used for restart purposes in the TPSS0 calculation, is written.

```
&global
project Porph
run_type energy
print_level medium
&end global

&force_eval
method quickstep

&dft
basis_set_file_name BASIS_MOLOPT
potential_file_name GTH_POTENTIALS

&mgrid
cutoff 300
ngrid5 5
&end mgrid

&qs
eps_default 1.0e-12
extrapolation aspc
extrapolation_order 5
&end qs
```

```
&scf
scf_guess atomic
max_scf 20
eps_scf 1.0e-6
max_diis 15
&outer_scf
max_scf 20
eps_scf 1.0e-6
&end outer_scf
&ot
preconditioner full_all
energy_gap 0.001
algorithm irac
minimizer diis
n_history_vec 20
&end ot

# this writes the converged GGA wavefunction to a file,
# which can later be reused
&print
&restart
filename =Porph-DFTGGA.wfn
&end restart
&end print
&end scf

&xc
&xc_functional tpss
&end xc_functional

# the smoothing here, requires to use the same cell
# geometry, if energies shall be compared
&xc_grid
xc_deriv nn10_smooth
xc_smooth_rho nn10
&end xc_grid
&vdw_potential
dispersion_functional pair_potential
&pair_potential
type dftd3(bj)
parameter_file_name dftd3.dat
d3bj_scaling 1.000 0.4535 1.9435 4.4752
&end pair_potential
&end vdw_potential
&end xc

# as we have a surface this time, we only use
# 2D periodicity
&poisson
periodic xy
poisson_solver analytic
&end poisson
&end dft

&subsys
# the cell size, needs to be precisely the one from
```

```
# the IC-QM/MM calculation
&cell
abc 24.469 24.469 25.0
periodic xy
&end cell
&topology
coord_file_name Porphyrine.pdb
coord_file_format pdb
conn_file_format off
&end topology

&kind H
element H
basis_set dzvp-molopt-sr-gth
potential gth-pbe
&end kind
&kind C
element C
basis_set dzvp-molopt-sr-gth
potential gth-pbe
&end kind

# we define two different types of nitrogen atoms:
# those which are sp2 hybridized, and those, which are
# sp3 hybridized, but treat them the same in the
# quickstep calculation
&kind N2
element N
basis_set dzvp-molopt-sr-gth
potential gth-pbe
&end kind
&kind N3
element N
basis_set dzvp-molopt-sr-gth
potential gth-pbe
&end kind
&end subsys
&end force_eval

&motion
&print
&restart_history on
&each
geo_opt 0
&end each
&end restart_history
&trajectory on
format xyz
&each
geo_opt 1
&end
&end trajectory
&end print

# geometry optimization using the BFGS optimization
# algorithm
&geo_opt
```

```
optimizer bfgs
max_iter 5000
&end geo_opt
&end motion
```

The next step is to do the geometry optimization using the TPSS0 functional with 25% Hartree-Fock exchange. Read in the TPSS wavefunction from the `Porph-DFTGGA.wfn` file and make the following changes to the `xc` section:

Listing 2: The new `xc` section for a TPSS0 calculation. Note the reduced amount of exchange for TPSS (`scale_x 0.75`), the `hf` section and the new DFT-D3 parameters.

```
&xc
&xc_functional
&tpss
scale_x 0.75
scale_c 1.00
&end tpss
&end xc_functional
&hf
fraction 0.25
&screening
eps_schwarz 1.0e-6
screen_on_initial_p .true.
&end screening
&interaction_potential
potential_type truncated
cutoff_radius 10.0
t_c_g_data t_c_g.dat
&end interaction_potential
&memory
max_memory 4000
eps_storage_scaling 0.1
&end memory
&end hf
&xc_grid
xc_deriv nn10_smooth
xc_smooth_rho nn10
&end xc_grid
&vdw_potential
dispersion_functional pair_potential
&pair_potential
type dftd3(bj)
parameter_file_name dftd3.dat
d3bj_scaling 1.000 0.4529 2.2382 4.6550
&end pair_potential
&end vdw_potential
&end xc
```

In addition to taking care of the correct definition of TPSS0 (TPSS with 75% exchange from the TPSS functional and 25% exchange from Hartree-Fock), we truncate the Hartree-Fock coulomb operator ($1/r_{12}$), to avoid self interaction errors due to non vanishing long range Hartree-Fock contributions, within the `interaction_potential` section.

Furthermore, as hybrid DFT takes much longer in the GPW [8] and GAPW [7] schemes, we

introduce a new approximation; the Auxiliary Density Matrix Method, which approximates the density matrix, by projection from a much smaller and highly decontracted basis. Not using this technique makes the TPSS0 calculation ≈ 100 times more expensive than the TPSS calculation. Using the Auxiliary Density Matrix Formalism [3] reduces the overhead to ≈ 4 times the cost of the TPSS calculation. Required changes to the input:

Listing 3: An additional auxiliary basis set file for ADMM basis sets needs to be added to the `dft` section. Also the flavour of the Auxiliary Density Matrix Methods needs to be specified.

```
basis_set_file_name BASIS_ADMM
&auxiliary_density_matrix_method
method basis_projection
admm_purification_method mo_diag
&end auxiliary_density_matrix_method
```

Listing 4: The `scf` subgroup of the `dft` section needs to be adapted to using a restart file. Furthermore, we specify a `print` section in the `dft` section, which writes cube files for the electron density and the electrostatic potential (called Hartree-Cube in *CP2K*).

```
wfn_restart_file_name GGAGuessGen/Porph-DFTGGA.wfn
&scf
scf_guess restart
max_scf 20
eps_scf 1.0e-6
max_diis 15
&outer_scf
max_scf 20
eps_scf 1.0e-6
&end outer_scf
&ot
preconditioner full_all
energy_gap 0.001
algorithm irac
minimizer diis
n_history_vec 20
&end ot
&end scf

&print
&v_hartree_cube
&each
geo_opt 1
&end each
stride 1 1 1
&end v_hartree_cube
&e_density_cube
&each
geo_opt 1
&end each
stride 1 1 1
&end e_density_cube
&end print
```

Listing 5: The atomic `kinds` need specification of the ADMM basis sets, used for the density matrix construction.

```
&kind H
```

```
element H
basis_set dzvp-molopt-sr-gth
potential gth-pbe
aux_fit_basis cpfit3
&end kind
&kind C
element C
basis_set dzvp-molopt-sr-gth
potential gth-pbe
aux_fit_basis cpfit3
&end kind
&kind N2
element N
basis_set dzvp-molopt-sr-gth
potential gth-pbe
aux_fit_basis cpfit3
&end kind
&kind N3
element N
basis_set dzvp-molopt-sr-gth
potential gth-pbe
aux_fit_basis cpfit3
&end kind
```

Run a geometry optimization with the input for TPSS0.

Run a vibrational analysis and calculate intensities on the optimized structures. Follow the scheme of GGA guess generation and ADMM production calculation as used for geometry optimization. Change the run type to `vibrational_analysis` and tighten the wavefunction convergence criteria.

Listing 6: Relevant changes and sections to the previous input for a vibrational analysis.

```
&global
project Porph
run_type vibrational_analysis
print_level medium
&end global

&vibrational_analysis
fully_periodic .false.
intensities .true.
nproc_rep 36
&end vibrational_analysis

&force_eval
method quickstep
&dft
&qz
eps_default 1.0e-16
...
&end qz

&scf
eps_scf 1.0e-8
...
```

```
&end scf
...
&print
&moments
periodic .false.
&end moments
&end print
&end dft
&end force_eval
```

2.2 Gold

To describe the gold surface, we use the Embedded Atom Method. [1] This force field method, especially made for metals and their alloys, allows for melting and dissociation – contrary to class I force fields – and is thus well suited for this system. The parameter file for EAM is complex and for the case of gold is luckily included in the *CP2K* distribution. First create a slab of gold with a 100-surface using *Avogadro*. Use "File" → "Import" → "Crystal" → "Gold" replicate the unit cell 10 times in x and y direction and 5 times in z direction, using "SStructure" → "SSuper Cell Generator", save the structure as a PDB file and note the cell parameters for the super cell shown in *Avogadro*. Write a *CP2K* input file for an optimization of this structure. Now that we optimize a crystal, we would need to optimize atomic positions and the cell vectors, but we will assume that the EAM doesn't differ too much from the experimental values.

Listing 7: *CP2K* input file for optimization for a gold slab with the EAM molecular mechanics method.

```
&global
project Gold
run_type geo_opt
print_level medium
&end global

&force_eval
# FIST is CP2K's force field module
method fist

# The mm section defines everything necessary for
# molecular mechanical calculations in FIST
&mm
# Define the forcefield
&forcefield
# All the gold atoms have partial charge of 0.
# In organic molecules this is seldomly the case
# but for EAM this is common
&charge
atom Au
charge 0.0
&end charge

# Force fields are evaluated using splined functions
```



```
# for efficiency and differentiation
&spline
# accuracy of the spline required
eps_spline 1.0e-5
&end spline

# The EAM only knows non bonded interactions, meaning
# that the bond can diffuse, contrary to harmonic
# potentials (bonded terms in class I force fields)
&nonbonded
# Define EAM interactions between the gold atoms.
# Note that the "Au.pot" file must be in the same
# directory as this input
&eam
atoms Au Au
parm_file_name Au.pot
&end eam
&end nonbonded
&end forcefield

# Poisson solver for long range electrostatic interactions
&poisson
&ewald
ewald_type ewald
gmax 25
&end ewald
# As we simulate a surface, we use 2D periodicity
periodic xy
poisson_solver analytic
&end poisson
&end mm

&subsys
# The x and y parameters are exactly the length of the
# 10x10 gold unit cell and in z we need enough space to
# keep the electron density away from the borders of the
# box in the QM/MM calculations of the next step
&cell
abc 24.469 24.469 25.0
periodic xy
&end cell
&topology
coord_file_name Gold.pdb
coord_file_format pdb
# For class 1 force fields, it is usually required to
# prepare topology information using external tools such
# as ANTECHAMBER. For EAM no connectivities are necessary
conn_file_format off
&end topology
&end subsys
&end force_eval

&motion
&print
&restart_history on
&each
geo_opt 0
```

```
&end each
&end restart_history
&trajectory on
format xyz
&each
geo_opt 1
&end
&end trajectory
&end print
&geo_opt
optimizer bfgs
max_iter 5000
&end geo_opt
&end motion
```

2.3 Porphyrine On Gold

Use *Avogadro* to draw a structure, with a porphyrine molecule flat and close to the gold surface in about 200 pm...300 pm distance to the surface atoms. The QM/MM setup needs description of the classical part (gold with the EAM, see section 2.2), the quantum mechanical part (GPW hybrid DFT, see section 2.1) and the description how these two parts interact. Therefore we need to define the image charge QM/MM formalisms, force field parameters for the non covalent interaction of gold with the porphyrine atoms (otherwise we would have purely electrostatical interactions) and which atoms belong to the QM and which to the MM part. We use interaction potentials in the form of Born-Mayer potentials with parameters taken from [9].

```
&global
project PorphOnAu
run_type geo_opt
print_level medium
&end global

&force_eval
# Use QMMM methods, which combine a DFT and a MM section
method qmmm

# Parameters for MM-QM interaction
&qmmm
# The QM cell may be a subcell of the complete simulation cell to
# save computational resources. This works well for "normal" QMMM
# simulations and the QM box should be centered around the QM atoms
# in the large MM cell, but for IC-QM/MM both cells need to have
# exactly the same size and position. Therefore do NOT center QM
center never

# QM polarizes MM not by point charges but by expansion of the
# charge density into 6 gaussians per atom
e_coupl gauss
nocompatibility
use_geep_lib 6

# The QM cell, needs to have same size as MM cell
```

```
&cell
abc 24.469 24.469 25.0
periodic xy
&end cell

# For each atomic kind, specify the indices of the atom, which are QM
# instead of MM atoms
&qm_kind H
mm_index 457 458 459 460 461 462 463 464 465 466 467 468 469 470
&end qm_kind
&qm_kind C
mm_index 433 434 435 436 438 439 440 441 442 444 445 446 447 448
mm_index 450 451 452 453 454 456
&end qm_kind
&qm_kind N2
mm_index 443 455
&end qm_kind
&qm_kind N3
mm_index 437 449
&end qm_kind

# The indices of the atoms in the MM part, which shall carry an
# image charge
&image_charge
mm_atom_list 1..432
# The image charge is a gaussian. It needs some extent
# but too much results in unphysical values
width 3.5
ext_potential 0.0
&end image_charge
&print
&image_charge_info on
&end image_charge_info
&end print
&end qmmm

# The DFT section is unmodified with respect to the porphyrine run
&dft
basis_set_file_name BASIS_MOLOPT
basis_set_file_name BASIS_ADMM
basis_set_file_name BASIS_ADMM_MOLOPT
potential_file_name GTH_POTENTIALS
&auxiliary_density_matrix_method
method basis_projection
admm_purification_method mo_diag
&end auxiliary_density_matrix_method

&mgrid
commensurate
cutoff 300
ngrid 5
&end mgrid

&qs
eps_default 1.0e-12
extrapolation aspc
extrapolation_order 5
```

```
&end qs

wfn_restart_file_name GGA-GuessGen/PorphOnAu-DFTGGA.wfn
&scf
scf_guess restart
max_scf 20
eps_scf 1.0e-6
max_diis 15
&outer_scf
max_scf 20
eps_scf 1.0e-6
&end outer_scf
&ot
preconditioner full_all
energy_gap 0.001
algorithm irac
minimizer diis
n_history_vec 20
&end ot
&end scf

&xc
&xc_functional
&tpss
scale_x 0.75
scale_c 1.00
&end tpss
&end xc_functional
&hf
fraction 0.25
&screening
eps_schwarz 1.0e-6
screen_on_initial_p .true.
&end screening
&interaction_potential
potential_type truncated
cutoff_radius 10.0
t_c_g_data t_c_g.dat
&end interaction_potential
&memory
max_memory 4000
eps_storage_scaling 0.1
&end memory
&end hf
&xc_grid
xc_deriv nn10_smooth
xc_smooth_rho nn10
&end xc_grid
&vdw_potential
dispersion_functional pair_potential
&pair_potential
type dftd3(bj)
parameter_file_name dftd3.dat
d3bj_scaling 1.000 0.4529 2.2382 4.6550
&end pair_potential
&end vdw_potential
&end xc
```

```
&poisson
periodic xy
poisson_solver analytic
&end poisson

&print
&v_hartree_cube
&each
geo_opt 1
&end each
stride 1 1 1
&end v_hartree_cube
&e_density_cube
&each
geo_opt 1
&end each
stride 1 1 1
&end e_density_cube
&end print
&end dft

&mm
# The MM part needs additional information, how the porphyrine
# atoms interact with the gold atoms.
# Every atom is neutral
&forcefield
&charge
atom H
charge 0.0
&end charge
&charge
atom C
charge 0.0
&end charge
&charge
atom N2
charge 0.0
&end charge
&charge
atom N3
charge 0.0
&end charge
&charge
atom Au
charge 0.0
&end charge

&spline
eps_spline 1.0e-5
&end spline

&nonbonded
&eam
atoms Au Au
parm_file_name Au.pot
&end eam
```

```
# These are generic Born-Mayer potentials, that can be estimated
# from atomic parameters. They describe van der Waals interactions
# between gold and porphyrine.
# Here the sp2 nitrogens and sp3 nitrogens are treated differently
&genpot
atoms Au H
function A*exp(-r/rho)-C/r^6/(1+exp(-20*(r/5.19 -1)))
variables r
parameters A rho C
values 0.48071 0.55936 0.0
rcut 15.0
&end genpot
&genpot
atoms Au C
function A*exp(-r/rho)-C/r^6/(1+exp(-20*(r/6.35 -1)))
variables r
parameters A rho C
values 24.22274 0.55936 54.429481
rcut 15.0
&end genpot
&genpot
atoms Au N2
function A*exp(-r/rho)-C/r^6/(1+exp(-20*(r/6.068 -1)))
variables r
parameters A rho C
values 24.22274 0.55936 63.138198
rcut 15.0
&end genpot
&genpot
atoms Au N3
function A*exp(-r/rho)-C/r^6/(1+exp(-20*(r/6.068 -1)))
variables r
parameters A rho C
values 14.708686 0.55936 20.030049
rcut 15.0
&end genpot

# These are completely flat Lennard-Jones Potentials for
# all QM-QM pairs. They do not contribute to the energy
# but CP2K is unhappy if they are omitted
&lennard-jones
atoms C C
epsilon 0.0
sigma 3.166
rcut 15.0
&end lennard-jones
&lennard-jones
atoms C N2
epsilon 0.0
sigma 3.166
rcut 15.0
&end lennard-jones
&lennard-jones
atoms C N3
epsilon 0.0
sigma 3.166
```

```
rcut 15.0
&end lennard-jones
&lennard-jones
atoms C H
epsilon 0.0
sigma 3.166
rcut 15.0
&end lennard-jones
&lennard-jones
atoms N2 N2
epsilon 0.0
sigma 3.166
rcut 15.0
&end lennard-jones
&lennard-jones
atoms N3 N3
epsilon 0.0
sigma 3.166
rcut 15.0
&end lennard-jones
&lennard-jones
atoms N2 N3
epsilon 0.0
sigma 3.166
rcut 15.0
&end lennard-jones
&lennard-jones
atoms N3 H
epsilon 0.0
sigma 3.166
rcut 15.0
&end lennard-jones
&lennard-jones
atoms H H
epsilon 0.0
sigma 3.166
rcut 15.0
&end lennard-jones
&end nonbonded
&end forcefield

&poisson
&ewald
ewald_type ewald
gmax 25
&end ewald
periodic xy
poisson_solver analytic
&end poisson
&end mm
```

```
&subsys
&cell
abc 24.469 24.469 25.0
periodic xy
&end cell
&topology
coord_file_name PorphyrineOnAu.pdb
coord_file_format pdb
conn_file_format off
&end topology

&kind H
element H
basis_set dzvp-molopt-sr-gth
potential gth-pbe
aux_fit_basis cpfit3
&end kind
&kind C
element C
basis_set dzvp-molopt-sr-gth
potential gth-pbe
aux_fit_basis cpfit3
&end kind
&kind N2
element N
basis_set dzvp-molopt-sr-gth
potential gth-pbe
aux_fit_basis cpfit3
&end kind
&kind N3
element N
basis_set dzvp-molopt-sr-gth
potential gth-pbe
aux_fit_basis cpfit3
&end kind
&end subsys
&end force_eval

&motion
&print
&restart_history on
&each
geo_opt 0
&end each
&end restart_history
&trajectory on
format xyz
&each
geo_opt 1
&end
&end trajectory
&end print
&geo_opt
optimizer bfgs
max_iter 5000
&end geo_opt
&end motion
```

Run a geometry optimization and a frequency calculation on the optimized structure. Do not forget to make the GGA guesses with TPSS!

Aufgabe 1 Questions

- Describe the Embedded Atom Method in your own words.
- Describe the IC-QM/MM method in your own words. Why does the QM box need to be as large as the MM cell?
- Calculate the adsorption energy.
- Plot the IR spectrum of the isolated porphyrine.
- Visualize the charge distribution of the image charges and discuss them together with the overall image charge induced.
- Visualize the symmetric and asymmetric valence and out of plane deformation N–H vibrations of the porphyrine for the isolated porphyrine and for the porphyrine adsorbed on gold. Compare the wavenumbers.
- Visualize the electrostatic potentials on the the isosurfaces of the electron densities for the adsorbed and the isolated porphyrine and discuss them.

Literatur

- [1] S. M. Foiles, M. I. Baskes und M. S. Daw. “Embedded-atom-method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys”. In: *Physical Review B* 33.12 (01/1986), S. 7983–7991. DOI: 10.1103/PhysRevB.33.7983.
 - [2] Dorothea Golze u. a. “Simulation of Adsorption Processes at Metallic Interfaces: An Image Charge Augmented QM/MM Approach.” In: *Journal of chemical theory and computation* 9.11 (11/2013), S. 5086–97. DOI: 10.1021/ct400698y.
 - [3] Manuel Guidon, Jürg Hutter und Joost VandeVondele. “Auxiliary Density Matrix Methods for Hartree-Fock Exchange Calculations.” In: *Journal of chemical theory and computation* 6.8 (08/2010), S. 2348–64. DOI: 10.1021/ct1002225.
 - [4] Marcus D Hanwell u. a. “Avogadro: an advanced semantic chemical editor, visualization, and analysis platform”. In: *Journal of Cheminformatics* 4.1 (01/2012), S. 17. DOI: 10.1186/1758-2946-4-17.
 - [5] Jürg Hutter u. a. “cp2k: atomistic simulations of condensed matter systems”. In: *Wiley Interdisciplinary Reviews: Computational Molecular Science* 4.1 (01/2014), S. 15–25. DOI: 10.1002/wcms.1159.
 - [6] Frank Jensen. *Introduction to Computational Chemistry*. John Wiley & Sons Ltd, 01/2007.
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- [7] Gerald Lippert, Jürg Hutter und Michele Parrinello. “The Gaussian and augmented-plane-wave density functional method for ab initio molecular dynamics simulations”. In: *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)* 103.2 (01/1999), S. 124–140. DOI: 10.1007/s002140050523.
 - [8] Gerald Lippert, Michele Parrinello und Jurg Hutter. “A hybrid Gaussian and plane wave density functional scheme”. In: *Molecular Physics* 92.3 (01/2010), S. 477–488. DOI: 10.1080/002689797170220.
 - [9] Stefania Rapino und Francesco Zerbetto. “Modeling the stability and the motion of DNA nucleobases on the gold surface.” In: *Langmuir : the ACS journal of surfaces and colloids* 21.6 (03/2005), S. 2512–8. DOI: 10.1021/1a047091o.
 - [10] Jianmin Tao u. a. “Climbing the density functional ladder: nonempirical meta-generalized gradient approximation designed for molecules and solids.” In: *Physical review letters* 91.14 (10/2003), S. 146401. DOI: 10.1103/PhysRevLett.91.146401.
 - [11] Thom Vreven und Keiji Morokuma. “Chapter 3 Hybrid Methods: ONIOM(QM:MM) and QM/MM”. In: Bd. 2. 01/2006, S. 35–51. DOI: 10.1016/S1574-1400(06)02003-2.
 - [12] A. Warshel und M. Levitt. “Theoretical studies of enzymic reactions: Dielectric, electrostatic and steric stabilization of the carbonium ion in the reaction of lysozyme”. In: *Journal of Molecular Biology* 103.2 (01/1976), S. 227–249. DOI: 10.1016/0022-2836(76)90311-9.
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