

Introduction to TURBOMOLE



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Basic Turbomole Facts

- ❑ Turbomole established by Prof. Reinhart Ahlrichs group from University of Karlsruhe in 1987.
Ahlrichs & co. *Chem. Phys. Letters* **1989**, 162, 165 > 5000 quotations.
- ❑ Copyrights hold by Turbomole GmbH. <http://www.turbomole.com/>
- ❑ Commercial code distributed by COSMOlogic company.
<http://www.cosmologic.de/>
- ❑ Only binaries sold, but source codes can be granted to external developers.
- ❑ Originally Linux/Unix & PC oriented, but now available versions for Windows & MacOS & many hardware platforms (IBM, HP, Cray, SGI).
- ❑ Turbomole is collection of various modules, each performing specific type of calculation. Most of these modules are parallelized (SMP, MPI).
- ❑ According to the authors "Turbomole is meant to be a production rather than an experimental code" - **most of the stuff implemented in Turbomole 'really work'.**

Turbomole Overview

- ❑ Gaussian basis sets.
- ❑ Electronic structure methods: **Hartree-Fock, Density Functional Theory;**
post-HF: **Møller-Plesset perturbation theory & Coupled Clusters.**
- ❑ Effective core potentials, including scalar relativistic effects for $Z > 36$.
- ❑ Analytical gradients for HF, DFT, MP2 & CC2. Analytical hessian for HF & DFT (+numerical for MP2).
- ❑ Geometry optimization & transition state search @ HF, DFT, MP2 & CC2.
- ❑ Excited state properties (vertical excitations, polarizabilities) & excited states geometry optimizations using time dependent DFT & CC2.
- ❑ NMR shieldings for closed shell molecules.
- ❑ Embedding molecules/clusters in periodic point charges (PEEC) or continuous polarizable medium environment (COSMO).

Turbomole Highlights

- ❑ Very fast & efficient factorization of Coulomb integrals in DFT & MP2 using 'resolution of identity' type (RI) algorithms.
 - ▶ RI-DFT about 40 times faster than 'normal' calculations. For systems with > 2000 basis functions MARIJ gives additional few times speed up.
 - ▶ RI-MP2 at least 5 times faster than regular MP2.
 - ▶ Also RI like algorithms for exchange integrals (efficient for very large basis sets).
- ❑ Efficient screening of 2-el. integrals - DFT cost scales as $\sim N^2$.
- ❑ Full use of all point groups, including non-Abelian (degenerated) ones. Calculations are roughly (*order of group*)x faster.
- ❑ Stable and accurate grids for integration of exchange-correlation terms.
- ❑ Low disk & memory requirements.

Functionalities in Development

- ❑ Periodic DFT calculations - for now (ver. 7.0) single point energy calculations only, *C1* point group & *P1* space group.
- ❑ Double correlated functional (both correlation & exchange orbital dependent) B2-PLYP - only energies now.
- ❑ Non-local density functional including vdW interactions - *C1* group & serial calculations.
- ❑ CCSD(T) - only energies & Abelian (non-degenerate) groups in a moment.
- ❑ CC & MP variants employing explicitly correlated 2-el. basis set functions (F12 family of methods) - usually energies only & limited implementations with point groups.
- ❑ & many other features included/refined in every new Turbomole release!

Turbomole Usage

Most Other QM Codes	Turbomole
One input file/job	One directory/job
All infos (coords, basis set, type of job) in input file.	<code>control</code> I/O file with references to external files. Type of job specified by external command.
Job started by calling one program.	Job started by calling one or more programs.
All calculations done in one step.	One type of calculations per call.
Output file(s) with results. Inputs unchanged.	<code>control</code> & output(s) with results. Input files (coord, orbitals) overwritten.

Turbomole Command Line Installation

- ❑ Optimal way - ask your favorite IT guy & don't bother anymore.
- ❑ After purchasing Turbomole from COSMOlogic download binaries - specified for your OS & hardware platform - in .tar.gz format:
- ❑ Unpack `tar -xvzf turbomole_70.tar.gz`
- ❑ `TURBODIR=/my_disk/my_name/TURBOMOLE`
`source $TURBODIR/Config_turbo_env or ..._turbo_env.tcsh`
add these 2 lines above to your setting file (like .bashrc).
- ❑ Important - set selected system resources at the machine where you run Turbomole:
check `ulimit -a`
data seg size/max memory size/stack size/virtual memory
should be set to unlimited/max. available memory
set limit -s hard, in csh/tcsh `limit stacksize hard`

The Most Important Modules

- define - input generator (text mode, largely self-explanatory)
- dscf/ridft - SCF HF/DFT (energy & wavefunctions) without/with RI.
- grad/rdgrad - HF/DFT gradients without/with RI. Converged dscf/ridft run required.
- mpgrad - MP2 energy & gradient. Requires successful dscf run.
- ricc2 - MP & CC energies, gradients & excited states properties employing RI. Successful dscf run required.
- escf - timed dependent & dielectric properties. Well converged SCF dscf/ridft run required.
- egrad - gradients & 1st order excited states properties. Well converged dscf/ridft & usually escf runs needed.
- mpshift - NMR shieldings for closed shell systems. dscf/ridft ...
- Example call - shell command: `ridft > myoutputfile`

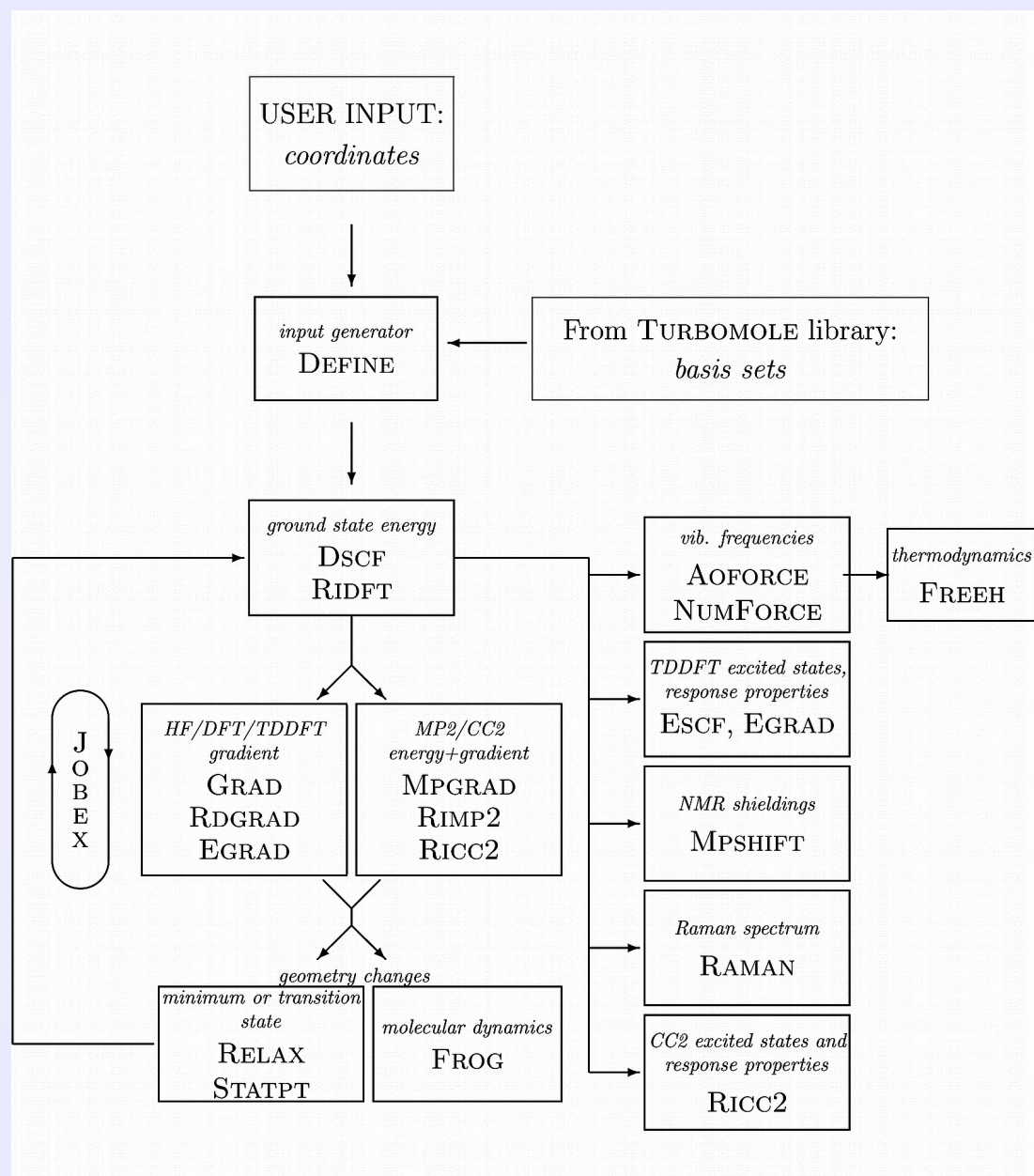
Still The Most Important Modules

- ❑ `relax` - geometry optimizer, proposes new structures on the base of gradients & updates Hessian. Gradients from either `grad`/`rdgrad`/`mpgrad`/`ricc2`/`egrad` mandatory.
- ❑ `frog` - molecular dynamics run. Gradients demanded as in `relax`.
- ❑ `statpt` - another geometry optimizer, can search for transition states (for the latter usually accurate Hessian needed).
- ❖ `relax/statpt/frog` in practice are called with `jobex` (see further)
script - shell command: `jobex -relax (-other options)`
- ❑ `aoforce` - analytical force constants, harmonic vibrational freqs. & IR intensities. Needs converged `dscf`/`ridft` (& for vibrational analysis well optimized geometry!).
- ❖ For methods without analytical Hessian implemented, (like MP2), 2nd derivatives can be always computed numerically from gradients with `Numforce` tool (see further).

Useful/Indispensable Tools

- ❏ `actual` - check actual step (use: `actual -r`)
- ❏ `cosmoprep` - setup of COSMO model of solvent by adding proper keywords to `control` file
- ❏ `eiger` - display orbital eigenvalues from orbital files
- ❏ `jobex` - Turbomole driver for all kind of molecular geometry processing (minima & transition states search, molecular dynamics)
- ❏ `Numforce` (capital N!) - numerical calc. of force constants, vibrational frequencies & IR intensities.
- ❏ `tm2molden` - prepare files readable by Molden graphical program (coords, orbitals, vibrational modes)
- ❏ `t2x` - convert Turbomole coord files to `.xyz` format
- ❏ `x2t` - convert `.xyz` files to Turbomole coord format
- 📦 `x2t myxyzfile > mycoordfile//t2x mycoordfile > myxyzfile`

Data Flows

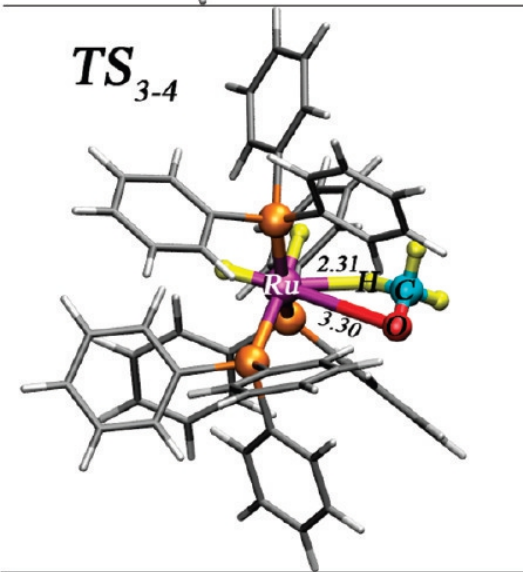
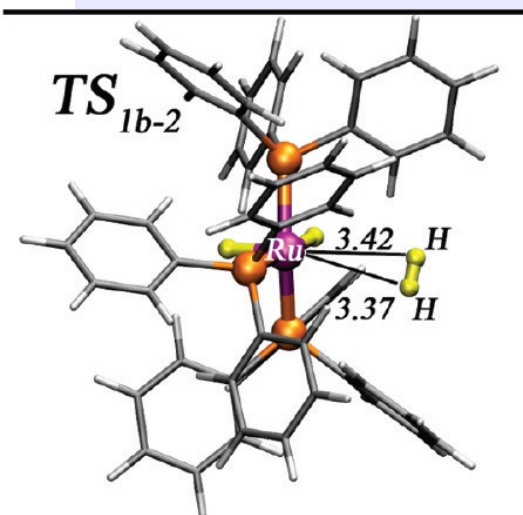


Turbomole @ Work - Real Molecules & Clusters

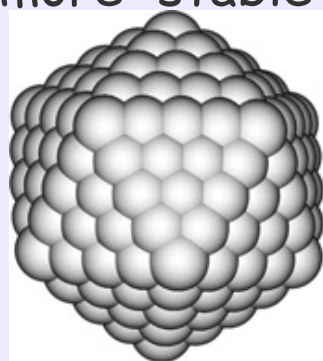
$\text{CH}_3\text{OH} \rightarrow \text{HCHO} + \text{H}_2$ by $\text{RuH}_2(\text{H}_2)(\text{PPh}_3)_3$: 4 competitive pathways

found, sterical effect of ligand responsible for higher selectivity to CH_3OH than to higher alcohols.

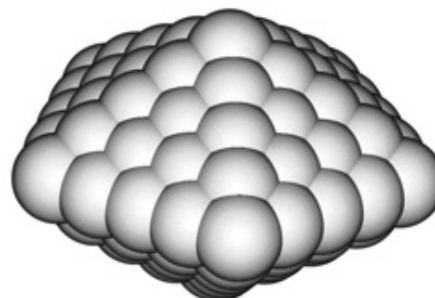
Sieffert & Bühl *J. Am. Chem. Soc.* **2010**, 132, 8056



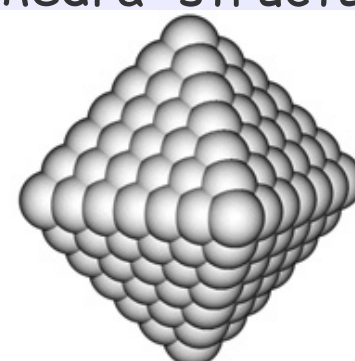
Pd clusters: Nava & co. *Phys. Chem. Chem. Phys.* **2003**, 5, 3372
fcc more stable than icosahedra & decahedra structures.



a) I_h Pd₃₀₉



b) D_{5h} Pd₁₀₅

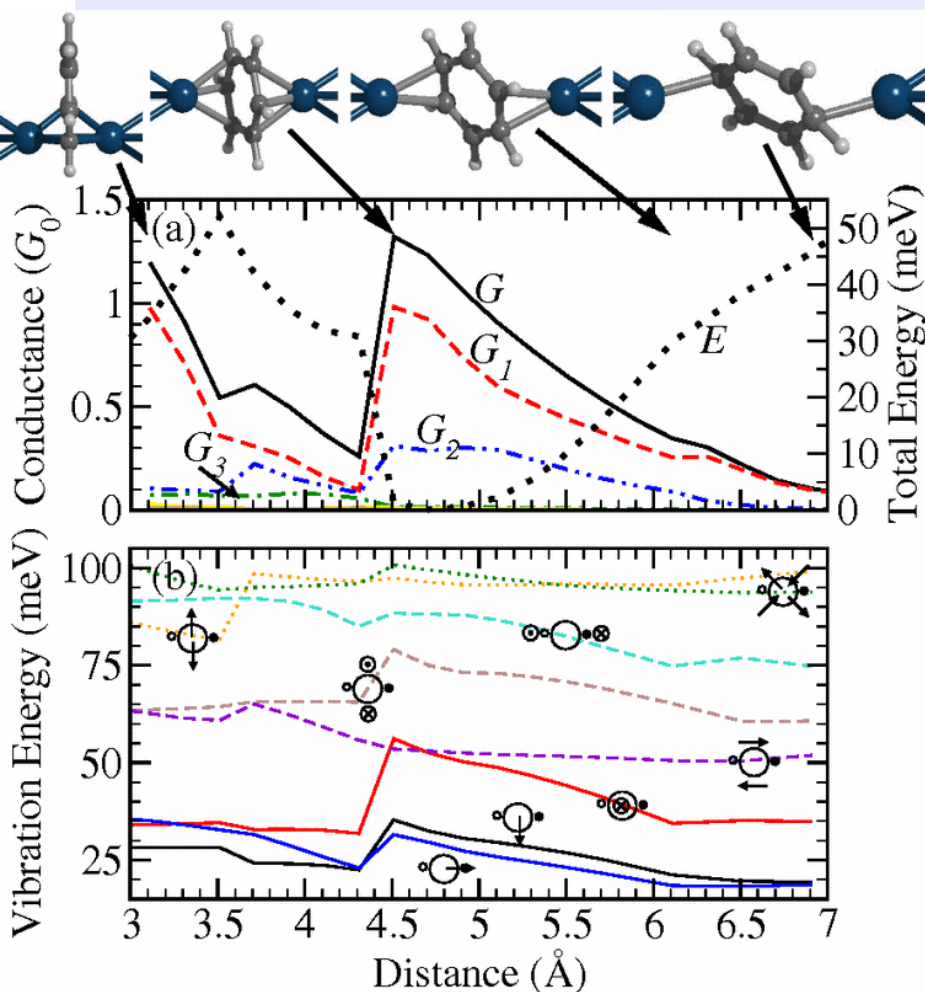


c) O_h Pd₂₃₁

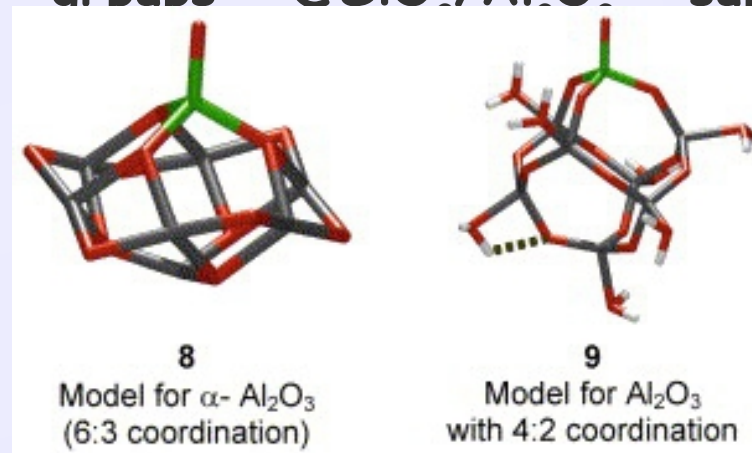
	Pd-Pd[Å]	$E_{\text{cohesion/atom}}$ [eV]
Exp.	2.748	3.59
DFT	2.816	3.90

Turbomole @ work – Part of Bigger Picture

- ▣ **Pt-benzene-Pt junction:** model consisting of 2 Pt₈ clusters connected with C₆H₆. Vibrational analysis performed to check how vibrations affect conductivity. Kiguchi & co. *Phys. Rev. Lett.* **2008**, 101, 046801



(V=O) arbuDs @SiO₂/Al₂O₃ support:



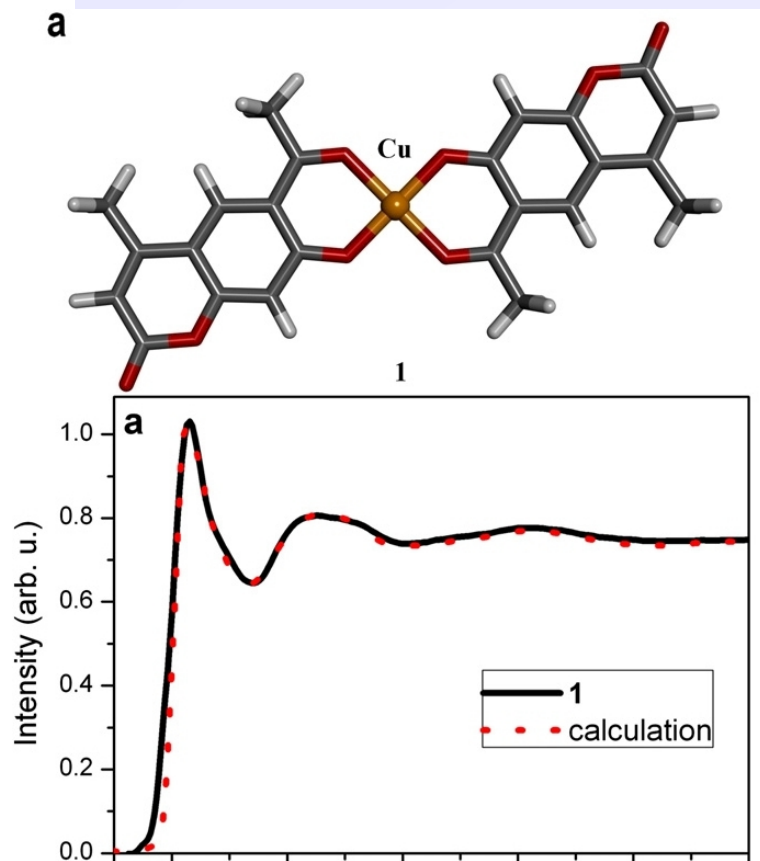
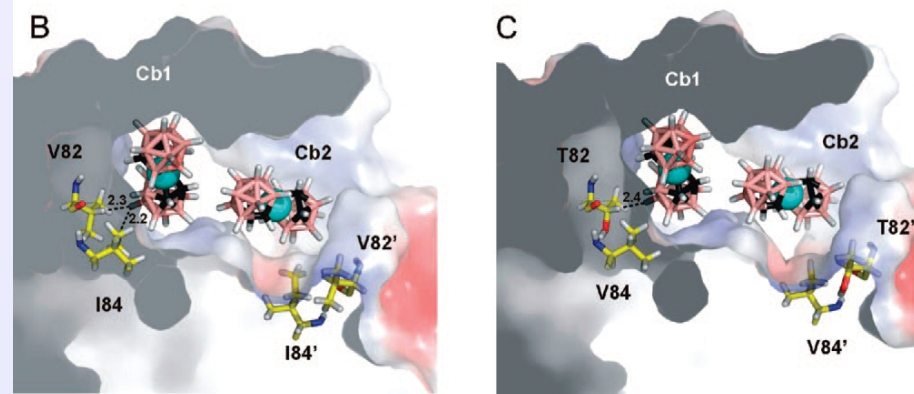
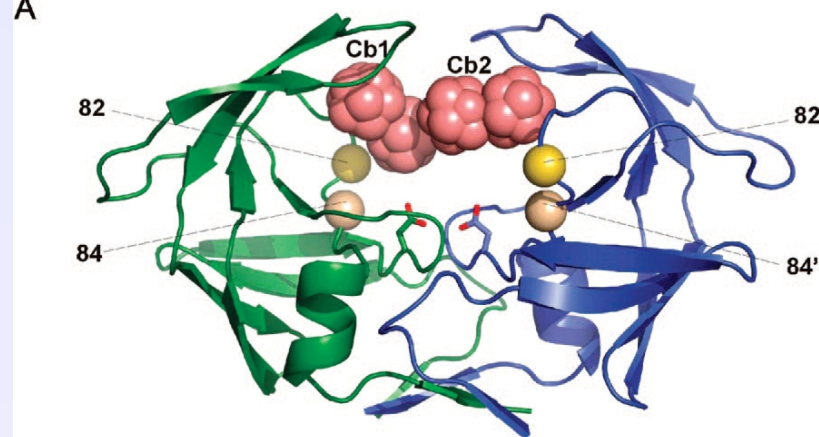
Revised interpretation of (V=O) IR spectra: they are support dependent & cannot be treated as indicator for monomeric/polymeric species.

Magg & co. *J. Catal.* **2004**, 226, 88

Turbomole @ Work – Medicine & Life Science

Co-carboranes as HIV protease inhibitors:
computations showed unusual dihydrogen
B-H...H-X bonds.

Kožíšek & co. *J. Med. Chem.* 2008, 51, 4839



**Cu-coumarin derivatives as anti-tumor/
-microbial drugs: DFT structure vs. XANES.**
Klepka & co. *J. Inorg. Biochem.* 2015, 145, 94

Turbomole & Pals

There are interfaces combining Turbomole with other programs to perform embedded cluster calculations QM/MM or QM/QM e. g.

ComQum = T + AMBER

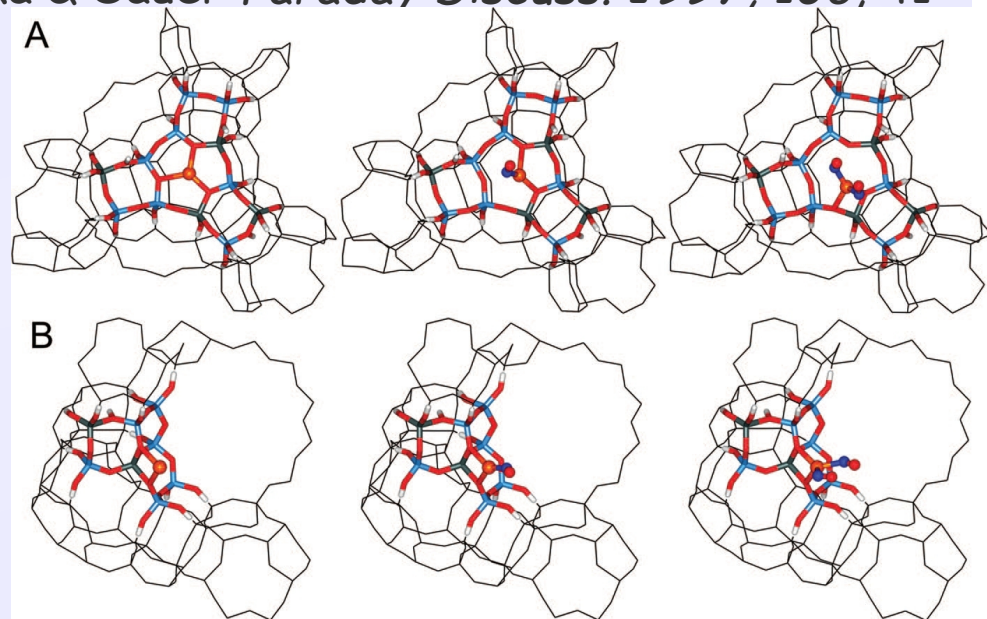
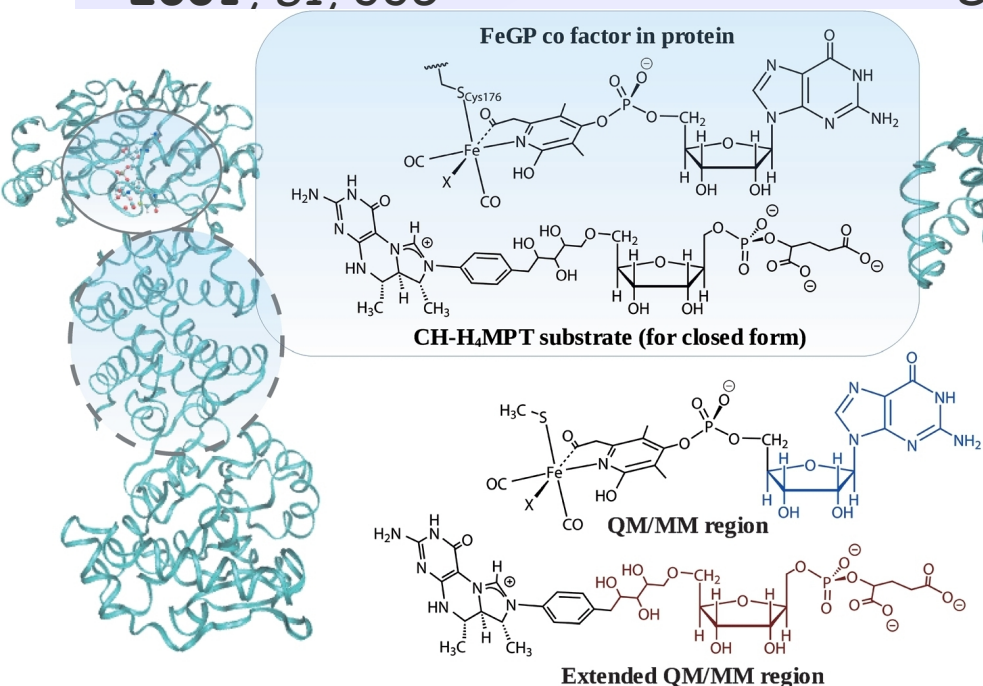
Ryde & Olsson *Int. J. Quant. Chem.*

2001, 81, 335

QMPot = T + GULP(periodic MM)/

+ Abinit (periodic DFT)

Sierka & Sauer *Faraday Discuss.* 1997, 106, 41



NO adsorption in Cu(I)-faujasite

Rejmak & co. *J. Phys. Chem. C* 2008, 112,

H₂ binding in Fe dehydrogenase

Hedegård & co. *Angew. Chem. Int. Ed.* 2015, 54, 6246

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For More Infos

➤ Manual

<http://www.turbomole-gmbh.com/turbomole-manuals.html>

Huge (over 400 pp.), luckily, you don't need to read all at once.

➤ Tutorial

Under the same link, 70 pp. nice intro two Turbomole.

➤ Turbomole forum

<http://www.turbo-forum.com/>

➤ Nice article in WIRE

<http://onlinelibrary.wiley.com/doi/10.1002/wcms.1162/full>

➤ Months/years your own practice with Turbomole:)

Thank you for your attention &

Marc Rodriguez for Turbomole installation.

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Exercises Plan

- 1. Preparing inputs for small closed shell molecules (e. g. ethanol), running geometry optimization & harmonic vibrational analysis, analysis & visualization of results. 2 sessions
- 2. Preparing of inputs for transition metal complex - case study of $[\text{Co}(\text{Im})_6]^{2+}$. Finding proper orbital occupations, converging SCF, low vs. high spin state, gradient vs. hybrid functional. 1 session
- 3. Calculating binding energy of van der Waals complex - case study of ethylene dimer. DFT-D vs. MP2, basis set superposition error, zero point vibrational energy. 1 session
- 4. Spectroscopy with Turbomole - vertical electronic excitations as approx. to UV-Vis spectra, Raman intensities, NMR shieldings. 1 session